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A TWO-CYCLE THEORY OF TROPICAL PEDOLOGY

C. D. OLLIER

(*Soil Survey of Uganda*)

Summary

Evidence from geomorphology and mineralogy is presented which indicates that many tropical soils in Uganda are formed on pre-weathered rock. The first cycle of weathering took place before the formation of the African surface, probably in Mid-Tertiary times or earlier. Further weathering and pedological change is taking place in the present cycle.

A variety of profiles are explained on this basis and some catenary relationships are also described. A number of previous ideas are discussed to indicate how the present theory differs from earlier ones.

Introduction

For the past three years the author has been concerned with a soil and geomorphology survey of Northern and Eastern Uganda, and a wide range of soils has been encountered. It has been found that the connexion between soils and geomorphology is most important in tropical soils, more so perhaps than in soils of temperate regions, where parent rock and parent material are often more nearly synonymous. From the literature it seems very probable that the relationships discovered in Uganda are also found in many other areas, and the ideas derived from a study of Uganda soils may have a wider application.

Many authors have described tropical soils and accounted for their features in various ways. Some of these ideas are incorporated in the following account, but it is impossible in a short paper to refer to all previous writers. Instead the position in Uganda will be described, and the ideas of some recent authors will be considered later.

The Present Theory

The fundamental idea in the theory propounded here is pre-weathering: present day soils are formed on pre-weathered rock. This is supported by evidence from geomorphology and mineralogy as well as pedology. A brief account of the geomorphology of Busoga District in Eastern Province, Uganda, is given below as an example of the evidence from that subject.

The highest summits of Busoga occur in the south and are remnants of an old peneplain (or other type of erosion surface) known as the Gondwana surface. This has been eroded by a later cycle which formed the African surface. There is a gradation between the surfaces as shown in Fig. 1, giving rise to three catenas, the Buganda, Buyaga, and Buruli. The African surface was cut across deeply weathered rock, and fresh rock outcrops in relatively small areas. The remnants of the Gondwana surface are almost entirely on quartzite which is highly resistant to weathering, and other rocks generally only outcrop as inselbergs or tors.

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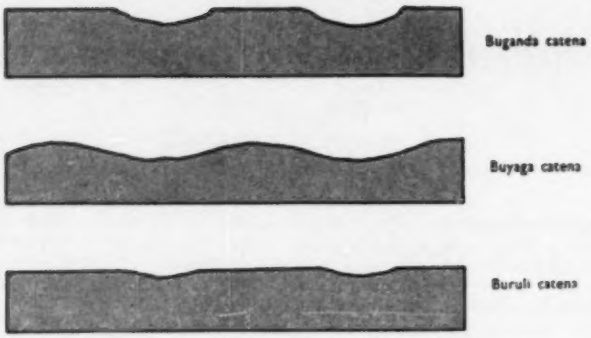

FIG. 1.

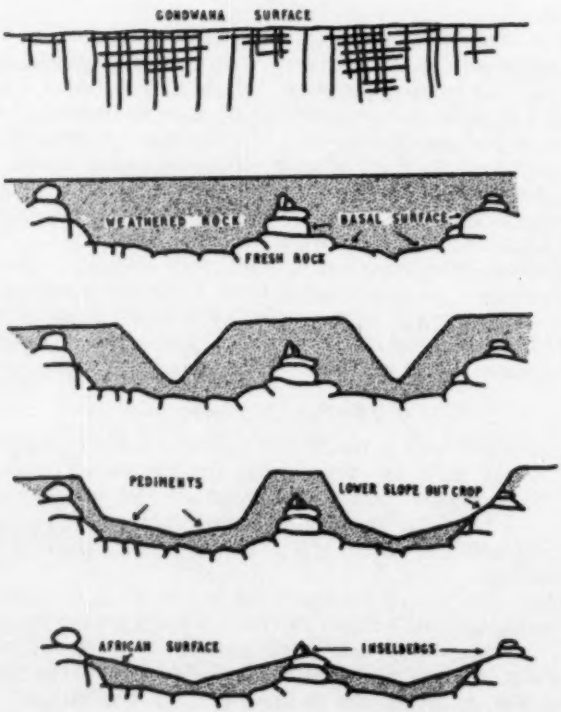

FIG. 2.

The postulated geomorphic history is shown in Fig. 2.

Very deep weathering took place below the Gondwana surface to form a thick layer of rotted rock. The junction between the weathered

rock and fresh rock is irregular but remarkably sharp, and is known as the basal surface of weathering, or simply the basal surface. The African cycle of erosion removed much of the rotted rock, but the base level of erosion was reached before it was all removed, and consequently the African surface is largely cut across rotted rock. Where the basal surface was reached by erosion, fresh rock emerges, usually as inselbergs or tors. This is the only satisfactory way to account for the observed fact that inselbergs of fresh rock are separated from each other by wide plains of rotted rock. The African surface is generally regarded as of End-Tertiary age, and as the weathering must have happened before this, it is Mid-Tertiary at least, and possibly very much earlier. The geomorphic history has been described in detail elsewhere (Ollier, *in lit.*).

From the pedological point of view the most significant feature of the geomorphic history is that erosion has exposed pre-weathered rock as the parent material on which soils could develop. A variety of such soils are described below.

Soil profiles of two-cycle origin

1. *Weathered rock to surface.* There are many sites, particularly on upper slopes, where rotted rock reaches the surface with very little modification. Quartz bands or other indications of rock structure reach the surface, and the only soil factors are slight eluviation of clay from the topsoil, and accumulation of a little organic matter.

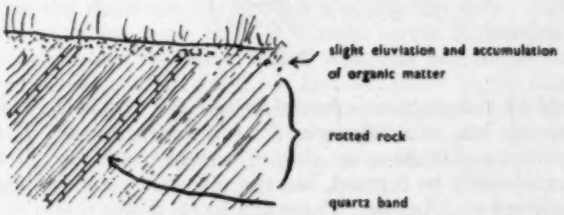

FIG. 3.

2. *Weathered rock, resorted at the surface.* These profiles are derived from those described above by sorting of the upper layers. Eluviation has been more intense and biotic activity has resulted in the breakdown of any rock structures in the top few feet of the profile.

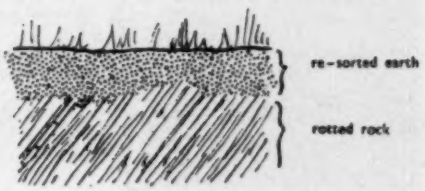

FIG. 4.

3. *Stone line profiles.* Profiles of this type are a special case of type 2 above, but are extremely common. It is necessary for quartz bands to be fairly frequent in the rotted rock, and for termites to be present. The termites build mounds above the surface, but cannot carry particles much above a millimetre in diameter, so coarse fragments and stones are left below. Eventually the mounds break down but new ones are made and the process continues until perfect layering is achieved. The upper layers of fine soil have been worked and reworked by termites and the stones accumulate as a stone line at the base of the zone of termite activity. Below the stone line there is, of course, weathered rock *in situ*. Other soil-forming processes are also active and there is some eluviation of topsoils, accumulation of organic matter, and sometimes lateritization as described below.

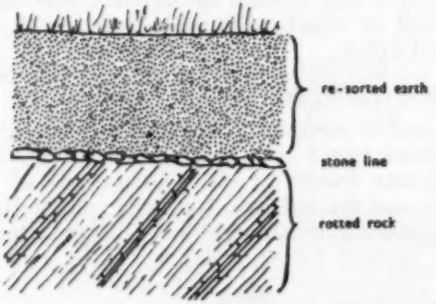

FIG. 5.

A variety of this profile is found where the rotted rock is a nearly amorphous regolith, and there are very few quartz bands. This happens especially on amphibolites or very micaceous schists. A thin stone line can occasionally be formed, but the soil above it looks just the same as the weathered rock below. There can be no doubt that it is weathered rock, for profiles go down for many tens of feet on sites which preclude drift.

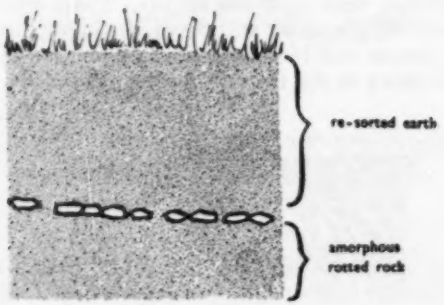

FIG. 6.

4. *Weathered rock with stone line at surface.* As in profile 3 above, the starting-point is rotted rock traversed by quartz bands. Sheet erosion removes the finer material, and coarse material accumulates on the surface, often as a layer of quartz stones. Such profiles are common in Karamoja, and elsewhere where there is poor vegetation cover and much erosion. Other soil-forming processes have little chance to act, and the profile is simply a stone line over rotted rock.

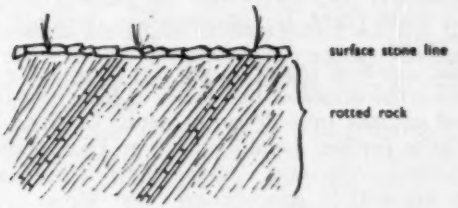

FIG. 7.

5. *Lateritized profiles.* Laterite (or ironstone concretions called 'murram' in Uganda) is formed by iron enrichment of certain layers in the soil profile and it occurs in regions with well-marked wet and dry seasons. Iron is leached out of upper layers of the soil in the wet season, carried both downslope and down the profile, and redeposited at depth when the soil dries out. The maximum concentration takes place where the drainage changes, and this most often coincides approximately with the stone line. If laterite forms in weathered rock *in situ* it is massive and vesicular, full of irregular hollow channels which are lined with layers of limonite. If laterite forms in the upper, sorted layers of the profile it tends to form murram pisoliths which may be cemented to form sheet laterite. The pisoliths do not show concentric banding. Murram and laterite often form a continuous sheet below the ground surface and parallel to it.

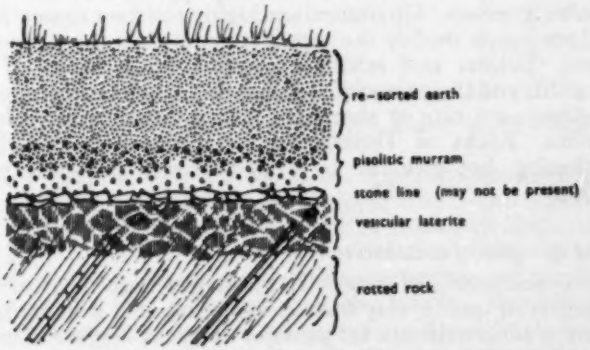

FIG. 8.

The process of lateritization is enhanced on flat sites, where thicker and more massive laterite is usually found. Well-preserved remnants of old erosion surfaces often have a thick cover. Erosion in a later part of the cycle may cause the laterite sheet to outcrop on valley sides. When it is exposed to the air it develops a skin of iron hydroxide and becomes much harder than it is in the ground.

Lateritization is a special phenomenon which can operate on many rocks and sediments. It complicates the present account, but is not relevant to the main point, for lateritization does not depend on pre-weathering of rocks.

6. *Drift soils.* Another factor which can complicate the soil profiles so far described is the occasional presence of hill-creep or other colluvial deposits. Most catenas provide no evidence of colluvial deposits and even on the slopes profiles usually appear to be sedentary. The slopes were graded before soils were developed from the underlying rotted rock and they are still in equilibrium. Any slope must be suffering slight erosion, but on many slopes in Uganda there is little evidence for it. Some lower slopes appear to have a rather large thickness of soil, which may be due to colluviation from the upper slopes, but there is rarely any definite evidence. Stone lines and derived laterite sometimes indicate drift movements.

The only well-marked drift soils occur round some large fresh rock outcrops, where debris derived from the fresh rock is spread out as an apron around the rocks. Here there is a profile with a topsoil rich in weatherable minerals overlying a subsoil of rotted rock from which virtually all weatherable minerals have gone.

7. *Other soil types.* It is not intended to discuss alluvial soils, soils formed on fresh rock in the present cycle, or other such types. These are obvious in the field, and do not affect the contention that a great many tropical soils are formed on pre-weathered rock.

Modification due to rock type

The processes outlined above are mostly applicable to areas of granite and granitic gneisses. Quartzites are highly resistant to weathering and form ridges which modify the topograpy and thus the arrangement of soil types. Schists and schistose gneisses have bands of different weatherability and their associated soils vary to some extent in accordance. Rock outcrops are rare or absent on highly weatherable rocks such as amphibolite. Rocks of Tertiary age or younger do not show deep pre-weathering, but give rise to straightforward one-cycle profiles of weathering.

The effect of zones of weathering

The pre-weathering of almost all rocks gave rise to a regolith consisting largely of quartz, clay (mostly kaolinite), and iron oxides. However, there is some evidence for zones of different degrees of weathering within the regolith, especially just above the basal surface. There one finds relatively weatherable minerals such as feldspar, micas, and

epidote are still present. This lower zone of weathering outcrops around fresh rock inselbergs, and soils here have a parent material which is slightly different from most pre-weathered rock.

Mineralogical evidence

Besides geomorphic evidence, there is mineralogical evidence to support the two-cycle theory of soil formation, and also demonstrate the sedentary nature of the soils. On a wide scale it is seen that kyanite is only found in soils developed from kyanite schists, garnet in soils developed from an originally garnetiferous rock, and so on. There is no evidence of widespread and much travelled drift or 'mantle' soils as described by Charter (1958).

To show the detailed use of mineralogy a brief account of one catena may be given. The whole catena has been described elsewhere (Radwanski and Ollier, 1959) and only the main features of the mineralogy will be summarized here. The data are shown in Table 1.

TABLE 1

		% feldspar in light fraction	*% magnetite in heavy fraction*	*Main nonopaque heavy minerals*
Shallow	0–3 in.	56	50	Z, T, E
	–10	45	50	Z, T, E, M
	–18	75	20	Z, T, E, M
	–36	72	50	Z, T, E, M, B
	–60	70	40	Z, T, E, M, B
	–72	75	60	Z, T, E, M, B
Red	0–3	0	5	Z, T
	–8	0	5	Z, T
	–18	1	10	Z, T
	–40	1	10	Z, T
	–60	1	20	Z, T
	–72	0	10	Z, T
Brown	0–3	0	5	Z, T
	–8	0	5	Z, T
	–20	6	5	Z, T
	–36	10	5	Z, T
	–60	6	5	Z, T
	–72	1	5	Z, T

Z, Zircon; T, Tourmaline; E, Epidote; M, Muscovite; B, Biotite.

Buwekula Shallow soils are found on upper slopes, usually around granite tors. Buwekula Red occurs on upper mid-slopes and Buwekula Brown on lower mid-slopes. It is seen that Buwekula Red and Brown are very poor in mineral species, while Buwekula Shallow, which has presumably suffered approximately the same amount of weathering in the present cycle, has a comparative abundance. According to the present hypothesis this can be accounted for by supposing that the parent materials of the Buwekula soils suffered pre-weathering, but Buwekula Shallow is formed on the lowest zone of the regolith, while

Buwekula Red and Brown were formed on the more intensely pre-weathered upper zones. Any one-cycle hypothesis of weathering must suppose that weathering has been much more intense on the mid slopes than on the upper ones, which seems very unlikely. The change in mineral proportions through the Buwekula Shallow profile gives some indication of the amount of weathering that has taken place in the present cycle.

The possibility of hill-creep modifying the profiles can be disproved. Drift from the rock outcrops on to Buwekula Shallow would enrich the top of the profile in weatherable minerals, but in fact it is found that the topsoil is depleted in weatherable minerals indicating weathering *in situ*. Drift from Buwekula Shallow on to Buwekula Red or Brown would contain considerable feldspar. In fact there is no feldspar in the topsoils of Buwekula Red or Brown.

Supposed two-cycle soils in other parts of Uganda often have a heavy mineral assemblage of opaques and a few zircon grains only. Supposed one-cycle soils on either fresh Basement Complex rocks of the Acholi surface, Tertiary volcanics or Plio-Pleistocene lacustrine sediments, all have a much richer mineral assemblage than two-cycle soils.

Catenas and other combinations of soil types

The kinds of soil profile described above occur in various combinations which constitute the soil-mapping units of the Uganda Soil Survey. Some of these are described below:

I. *Catena with rock outcrops.* There are rock outcrops on the hill top. At 1 there are soils formed on the lowest zone of weathering which

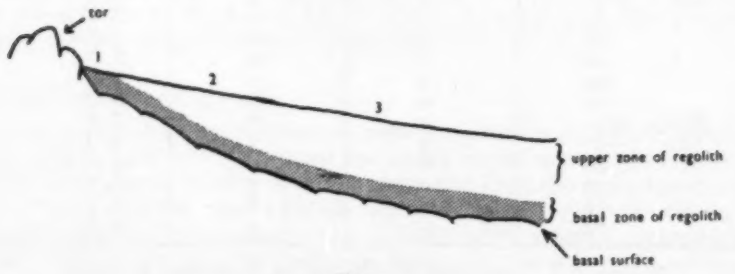

FIG. 9.

contains some weatherable minerals. There may be a drift of debris derived from the fresh rock of the outcrop in some instances. At 2 there is highly weathered rock as the parent material. There may be resorting of the upper part of the solum and a stone line or murram may be present. Profiles at 3 are very much the same as 2 but there may be some colluvium. Alluvial associates usually occur farther downslope. Complications in the catena may occur if there are lower slope outcrops, which lead to a repetition of upper-slope profiles on the lower slopes.

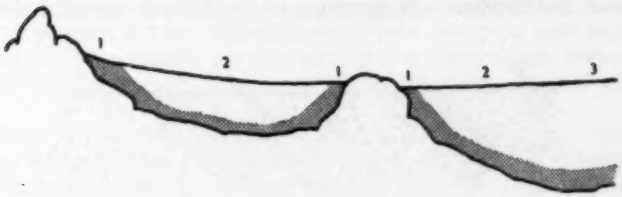

FIG. 10.

II. *Catenas without rock outcrops.* These occur mainly in watershed areas.

FIG. 11.

At 1 there is weathered rock almost to the surface and usually only a little sorting of the upper solum. At sites 2 and 3 the profiles are exactly as in the first catena described. A variation of this catena occurs where a remnant of a former erosion surface is preserved as a hill top.

FIG. 12.

This will usually have a laterite cap, and the remains of the soil above the laterite are often truncated. The lower part of the catena is unaffected.

III. *Soils developed on plains of advanced erosion.* Many parts of the African surface in Northern Uganda are well-developed plains, and very flat, but 6n these are sedentary red soils similar to those on lower slopes in areas of more marked relief. It sometimes happens, however, as in the southern part of West Nile district, that a new cycle of erosion cuts across the rocks at such a low level that almost all the weathered rock is removed and a new surface (the Acholi surface in this case) is cut across mostly fresh rock. On the fresh rock surface sedentary, juvenile soils have formed. There is almost always some pre-weathered rock, following bands of certain petrology, generally micaceous; on this are found the two-cycle soil types. This arrangement is not a catena, for the soil pattern depends on geology and there is no repetitive

pattern of distribution. Diagrammatically the soil variation looks like this:

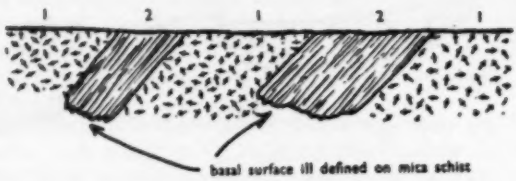

FIG. 13.

At 1 is skeletal soil over hard fresh rock.
At 2 is somewhat resorted soil over pre-weathered rock.

Discussion

A few previous accounts of tropical soils will now be discussed to show how they differ from the present thesis.

Greene (1945) described red-loam catenas on pre-weathered rock formed in Miocene times, thus anticipating the theory presented in the present paper. His pre-weathering catenas are characterized by remnants of erosion surfaces with ironstone, as in Fig. 12 above. He also describes a red-loam catena similar to catena II, Fig. 11 above, which is believed to be formed directly on acid crystalline rock. From the description of this catena it could be fitted into the present theory, but it is possible that a one-cycle soil might reach this high degree of weathering under suitable conditions. It is said that the red loams of the two catenas are apparently identical.

Charter (1958) described some soils of southern Tanganyika. His diagrams show soil profiles of the same types described here, but he believed that the soils were drift soils. He says, '. . . the upland soils . . . are *not*, as previously assumed, developed directly by the weathering in place of the underlying bedrock. They are, instead, derived from a mantle of red earth of varying thickness which overlies, and had its origin from, the rocks of the basement complex. This relationship between mantle and bedrock is analogous to that which exists in the northern parts of the temperate zone. There one has mantle rock derived, by glacial attrition and transport, from the underlying bedrock and it is on the surface of this mantle that the soils are developed.'

He described the weathered rock as 'mantle' and it might seem, from his Fig. 1 and some of the text, that this is the layer of pre-weathered rock of the present account. However, he later makes it clear that he is referring to the soil above the stone line, and in his diagrams marks the layer below the stone lines as 'weathered surface of bedrock' and 'more or less unweathered bedrock'. Charter also believed that stone lines were formed at the ground surface and were later buried by the mantle.

The main difference between Charter's account of profile development and the present one is that he thinks the upper soil is transported. He has some evidence for this, but in Uganda most soils have proved to

be sedentary when investigated by mineralogical methods. Charter did not try to account for the distribution of rock outcrops and weathered rock; nor did he consider pre-weathering very important, although he supposed there had been a change of climate since his 'mantle' accumulated.

Anderson (1957) described many soils derived from very weathered rock, and follows Milne (1947) in believing that the depth of weathering could not be produced by present rainfall, and that soils over about 2 metres are 'fossil relics' of a wetter period in the past. No suggestion is made of how much past, but in the present paper the period of great weathering is pushed back at least to a time before the African surface was developed, probably Mid-Tertiary. Anderson believes stone lines are due to termite activity but suggests that soils with over 2 metres of earth above the stone line are probably 'mantle soils'. He seems to consider the movement of the mantle much less than Charter supposed, and the present writer has no objection to such small movements.

Nye (1954) described a catena very like catena number I in the present account. He does not attempt to account for weathered rock being the parent material of the soils, or for the occasional presence of rock outcrops. He attributes the upper soil to the activity of soil fauna, but believes that soil creep is nevertheless important, even on slopes of only 5 per cent.

Spurr (1954) described an area of composite topography in Tanganyika. He gives no detailed profile descriptions, but the profiles seem to be like those described by the other authors referred to, and generally underlain by deep pre-weathered rock—now usually kaolinitic red earths or ferralites.

Spurr believes that the deep weathering is a continuous process, and as each new erosion level is produced it undergoes deep weathering. This gives rise to a flight of erosion levels, all having soils of similar type but of different age. According to the present account the deep weathering took place at the time of the oldest erosion level, and successive erosion cycles bevelled new surfaces across the pre-weathered rock. The result is the same in either case.

Although Spurr believes in a continuous process of weathering he does say that '. . . where topsoils do exist, although they have admittedly been formed under present vegetal and climatic conditions, the material from which they have developed is often soil material which had its origin in past erosion cycles as part of a former catena. Sub-soils over thirty feet in thickness are common where weathering has been deep and continuous, or where a soil has developed from transported material which itself lies deep on bedrock. The development of these sub-soils has been very little affected by their present-day environment.' He believes this is only a local complicating factor, but it is the very essence of the thesis of the present paper.

Spurr describes Pleistocene and recent levels which, like their Acholi surface equivalent in Uganda, have skeletal and freely drained soil formed in the present cycle. He presumably attributes this to lack of time to form a soil such as occurs on the older surfaces. In the present

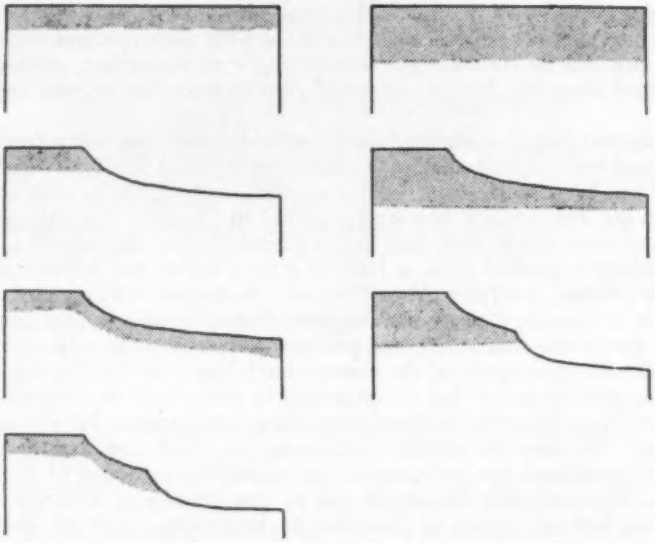

FIG. 14. Evolution of multiple surfaces according to Spurr (left) and the present account (right).

account it is believed that erosion has reached a level below the basal surface of the pre-weathered rock. The evolution of the lowest surface of Fig. 14 above shows this diagrammatically.

Acknowledgements

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REFERENCES

ANDERSON, B. 1957. A Survey of Soils in the Kongwa and Nachingwea Districts of Tanganyika. University of Reading.

CHARTER, C. F. 1958. Report on the environmental conditions prevailing in Block 'A', Southern Province, Tanganyika Territory. Ghana Dept. Agric. Occ. Pap. No. 1.

GREENE, H. 1945. Classification and use of tropical soils. Proc. Soil Sci. Soc. Amer. **10**, 392–6.

MILNE, G. 1947. A soil reconnaissance journey through parts of Tanganyika. J. Ecol. **35**, 192–265.

NYE, P. H. 1954. Some soil-forming processes in the humid tropics. I. A field study of a catena in the Western African forest. J. Soil Sci. **5**, 7–21.

OLLIER, C. D. Etchplains and inselbergs in Uganda. (In the Press.)

RADWANSKI, S. A., and OLLIER, C. D. 1959. A study of an East African catena. J. Soil Sci. **10**, 149–68.

SPURR, A. M. M. 1954. A basis of classification of the soils of areas of composite topography in central Africa, with special reference to the soils of the southern highlands of Tanganyika. Second Inter-Afr. Soils Conf. **1**, 175–90.

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A STUDY OF AN EAST AFRICAN CATENA

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(*Soil Survey of Uganda*)

Summary

The Buwekula catena occupies a tor landscape which was formed in two stages, as in Linton's two-cycle theory. Weathering under present conditions has been traced from the proportions of minerals. Feldspar and magnetite show weathering trends and among non-opaque heavy minerals there is an order of weatherability in the series biotite, muscovite, and epidote.

The soil sequence from summit to valley is as follows. Buwekula Shallow occurs on the upper slopes and is a comparatively youthful soil. Buwekula Red occurs on the upper and middle sections of pediments and is a deeply and thoroughly weathered soil the parent material of which has sustained more than one cycle of weathering. Buwekula Brown is a topohydric variant of Buwekula Red and occurs in the lower sections of the pediments. Two alluvial series (Buwekula Yellow-Brown and Buwekula Grey) are derived from weathering and erosion products of the deeply weathered upland associates.

Mineralogical and geomorphic evidence indicates that much weathering took place before the present land surface evolved and that the upland soils are being formed to a large extent on pre-weathered material. Since the formation of the present land surface further weathering has given rise to the present soil profiles which appear to be in equilibrium with their environment, so that the development of soil horizons is keeping pace with all the processes responsible for their removal.

The distribution of individual soil series of this catena has a considerable influence on the land-use pattern of the area. Despite the ample and favourably distributed rainfall the Buwekula soils are not as productive agriculturally as some other soils in Uganda under similar climate. The main reasons for this are their high acidity associated with extremely low percentages of base saturation and their liability to accelerated erosion.

Introduction

SINCE Uganda can be claimed as the type locality of soil catenas (Milne, 1935 and 1936), these natural mapping units have been used wherever possible in the reconnaissance soil survey of the Protectorate. In this paper we describe the whole of the Buwekula catena, which occurs over an area of about 1,100 square miles in south-western Uganda (Fig. 1).

Geology and Geomorphology

The Buwekula catena covers a region of rugged topograpy with an average altitude of about 4,000 ft. with a relative relief around 300 ft. The area is underlain by post-Karagwe-Ankolean granite. Where exposed this is often a very coarse rock consisting of large feldspar and quartz crystals, with subsidiary muscovite. Biotite is uncommon and all other minerals very rare. Many tors are composed of giant porphyry granite, but it is possible that the inter-tor areas, now occupied by weathered rock, were originally of finer grain than the outcropping fresh rock.

Granite outcrops as rounded hills and tors all over the district and

quite a high proportion of the land surface is bare rock. Most of the rock exposures are on ridge tops, but they are also frequent on lower slopes. The general appearance of the country is shown in Plate I.

FIG. 1

Between the outcrops there is intensely weathered rock, often to a great depth. Quartz veins traverse the rotted rock, showing that it is *in situ*, and there are other features to show that the original rock structure is retained, although weathering has altered many of the original minerals. The quartz is less weatherable than other minerals and consequently the weathered rock always contains much angular quartz of fine gravel size.

There is a remarkably sharp junction between weathered and fresh rock, extending over only a few inches. Boulders or 'core stones' are sometimes detached from the main rock mass, and these too have a very sharp junction with the surrounding rotten rock. Such a sharp junction is shown in Plate II.

The weathered rock can be divided into zones. The lower one retains much rock structure, and may contain unweathered core stones. The zone above is uniformly red, and although there is evidence from quartz bands, &c., to show that it is *in situ*, this is not apparent in all sections.

Modern hypotheses for the formation of tor landscapes (Linton, 1955; Waters, 1958) can be applied to the Buwekula area. Briefly its geomorphic history appears to be as follows: The granite was planated by the Gondwana erosion surface, which was very well developed and existed for a very long time with little change. Weathering went on beneath this senile erosion level and picked out the structures, attacking especially the finer grained, well-jointed, and most fissile parts. It seems

to be a characteristic of such deep weathering to form a sharp junction between fresh and weathered rock and this junction has been called the 'basal surface of weathering' (Ruxton and Berry, 1958). It also seems to be typically irregular.

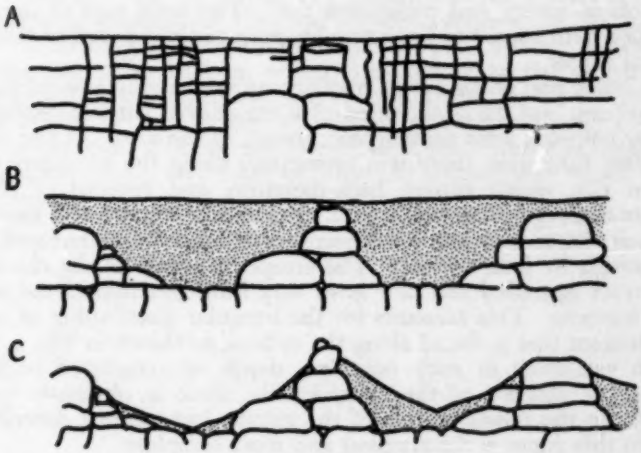

FIG. 2

Eventually a new cycle of erosion was initiated and a dendritic drainage system flowing west was incised on to the old surface. This drainage system became adjusted to structure and eroded the most weathered rock, leaving fresh rock to outcrop as tors and the present landscape of granite hills with a cover of rotten rock on slopes. Such a surface may be regarded as a kind of 'etchplain' (Wayland, 1934). The hills tend to reach the same approximate altitude but there are very few certain remnants of the original Gondwana peneplain. The sequence of events is shown diagrammatically in Fig. 2, A–C.

From a pedological point of view the most important feature of this history is that the weathered rock is a remnant of a previous cycle of weathering. The weathering which formed the parent materials for the present-day soils took place in Tertiary times. Weathering in the current cycle could only take place after the formation of the present-day slopes.

There is, of course, no evidence for any break in weathering, but there is a distinct break in the erosional history—the very perfect Gondwana surface existed for a very long time before its dissection by the later cycle of erosion. It is simply maintained that most of the weathering which converted the parent rock into soil material took place before erosion formed the present land surface, although there is mineralogical evidence, given later, for some contemporary weathering.

The angles of hill slopes seem to be partly controlled by the basal

surface of weathering and partly by the processes which formed them. The cross-section shown in Fig. 3 bears out an impression gained in the field that most of the slopes are almost straight. The slope angle is about 9–10°. Pallister, in his study of Buganda slopes (1957), reported similar straight slopes. He found that hill slopes (*sensu stricto*) had gradients of 20–28° and pediments 5–8°. The main part of the slopes described here appear to be unusually steep pediments rather than free-face hill slopes.

The lower part of the catena may or may not have an alluvial member or members, and the distribution of these alluvial patches results from a rather complex later geomorphic history of the area. At the time of rift valley formation there was upwarping along the boundary of the western rift, which caused back-damming and reversal of the old westerly drainage (Wayland, 1921). The minor streams still flow west, but their flatter portions have been aggraded to form terraces, since cut through by later erosion. The steeper portions of the old valleys were never aggraded and now have very little alluvium in the narrow valley bottoms. This accounts for the irregular distribution of swamp and alluvium that is found along the valleys, as shown in Fig. 4.

With variations in rock outcrops, depth of weathered rock, and presence or absence of the alluvial soils, there is obviously quite a variation in the possible form of the catena, but the one described in detail in this paper is the simplest and most complete.

Climate

The average annual rainfall is about 45 in. in the west, increasing to just over 50 in. in the east of the area. There are two rainy peaks, in March–May, and in October–November, with the intervening short dry season in June–July and a long one in December–February. Light showers are common in the dry season with the average monthly falls seldom less than 2 in. The average annual temperature as recorded on Mubende Hill (5,000 ft.) is 66·8° F. with the maximum of 82·2° F. at the peak of the dry season and minimum of 58·2° F. in the rainy season. The relative humidity of the air at 8.30 a.m. is fairly constant, the average being 80 per cent. At 2.30 p.m. it drops to an average of 65 per cent.

Vegetation

The present natural vegetation consists of savanna with scattered trees and shrubs. In more remote and rarely cultivated areas there is a tendency to forest regrowth with the resulting invasion of thicket or young secondary forest. The latter usually occurs along valley fringes and, if undisturbed, extends gradually into the upland soils. Swamp communities consisting of papyrus (*Cyperus papyrus* L.) or *Miscanthidium violaceum*, K. Schum. (Robyns) are commonly found on the floors of larger river valleys.

On the transect line along which soil pits were dug there was a

narrow belt of *Themeda triandra* Forsk., surrounding the rocky outcrop on the hill summit and followed by a grass savanna with frequent scattered shrubs extending down to the valley bottom. The dominant grasses were *Cymbopogon excavatus*, Stapf., *Brachiara soluta*, Stapf., and *Brachiara brizantha*, Stapf. The most numerous species of shrubs were *Vernonia amygdalina*, Del. and *Vernonia uniflora*, Hutch. & Dalz. There was no marked change in the dominant plant species between the hill slope and valley bottom, owing, presumably, to the fact that the adjoining valley was relatively narrow and possessed an intermittent stream capable of only occasional flooding for short periods. Together with the species already mentioned, scattered *Loudetia kagarensis* Hubbard ex Hutch. and some unidentified sedges were found in the valley bottom.

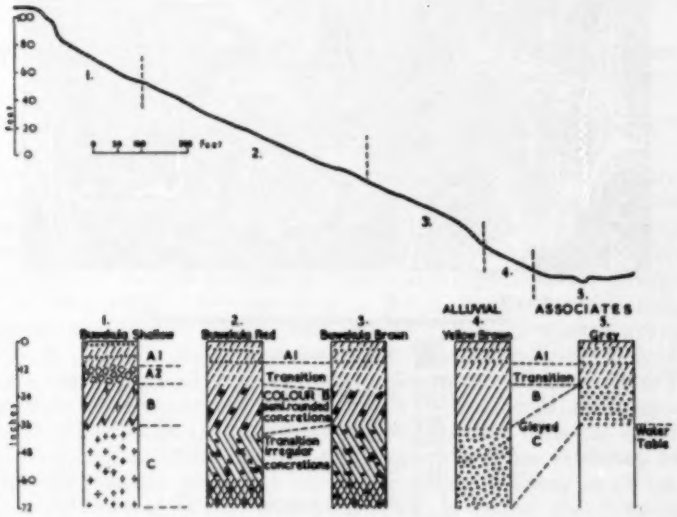

FIG. 3.

The Buwekula Catena

Fig. 3 represents a full topographic soil sequence from summit to valley. There are three upland- and two lowland-alluvial components in this catena each distinguished at the soil series level. These series are classified according to their present topographic site and the resulting profile morphology. A compound soil series name is used, consisting of the catena name with an adjective describing an outstanding characteristic of the soil series. By applying this system the usage of a number of local names is reduced and each soil name is made to convey something of its actual character in the field.

Each profile diagram represents an individual soil profile as found on a given topographic site. The boundaries between the soil series vary considerably in their sharpness. There is usually a fairly sharp boundary

between Buwekula Shallow and Buwekula Red, but the latter merges in Buwekula Brown through a number of intergrades. Again, the boundary between Buwekula Brown and the alluvial soils is clearly defined by topography, but the two alluvial members gradually merge into each other.

Fig. 4 (a generalized portion of the soil map) shows the areal expanse

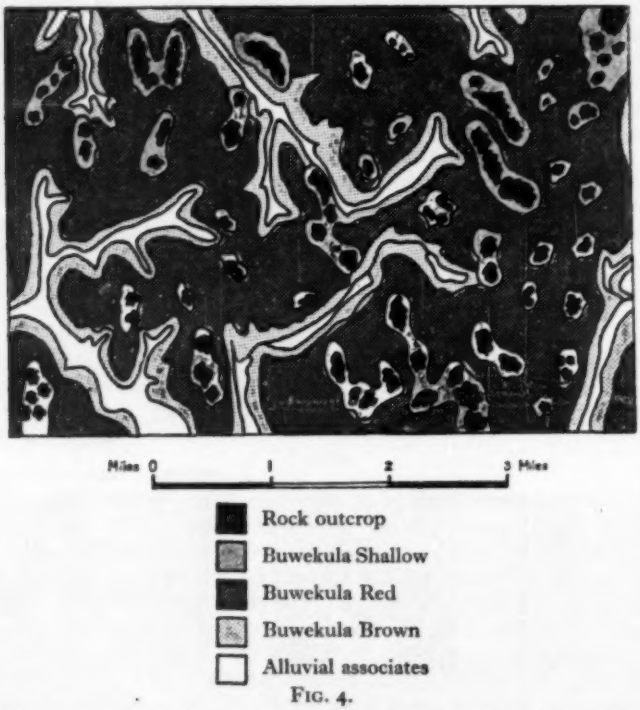

FIG. 4.

of the component soil series originally mapped at the scale of 1:50,000. The two alluvials are mapped together since the extra field work involved in separating them would not have been justified on the present scale.

The full catenary sequence as shown in Fig. 3 has not developed uniformly over the whole area and quite frequently one or more of its component soil series are absent. The reasons for such irregularity must be sought in the composition of the parent rock, which shows a varying degree of resistance to weathering, and in the complicated geomorphic history already described.

In the following sections the individual soil series will be described in detail and their morphological and analytical properties discussed from the point of view of pedogenesis. These are actual profiles from a transect studied in the field.

Buwekula Shallow. This series occurs on the upper slopes of hills

and forms a relatively narrow belt surrounding the rocky summits. The term 'shallow' refers to the presence of incompletely weathered rock at shallow depths though the upper horizons are usually well developed but not sharply defined. The profile is described below:

0–3″ Dark grey (10 YR 4/1).* Humose, loamy sand with frequent coarse angular quartz gravel. Weakly crumbly and loose. Frequent roots.

3–10″ Dark brown (7·5 YR 4/2) less humose, loamy sand with very frequent coarse angular quartz gravel and frequent stones. Weakly crumbly and firm. Frequent roots.

10–18″ Light brown (7·5 YR 6/4) slightly stained with humus, loamy sand with abundant coarse angular quartz gravel. Frequent stones. Structureless and firm.

18–36″ Reddish-yellow (7·5 YR 6/6) loam+frequent quartz gravel and stones+occasional small fragments of feldspar+occasional minute flakes of muscovite. Slightly compact. Breaks into subangular blocks of varying stability.

36–60″ Yellow-red (5 YR 5/6) gravelly clay-loam+abundant angular quartz stones +frequent fragments of feldspar and flakes of muscovite. Structureless and compact.

60–72″ Yellow-red (5 YR 5/8) similar to the above+more frequent fragments of partially weathered rock.

Applying the standard horizon nomenclature, the first 0–3-in. layer would correspond to the A_1 horizon in which humus is intimately mixed with mineral matter. The second 3–10-in. layer may be regarded as an extension of the A_1 horizon. It is essentially similar to the overlying layer in its high content of humus and represents a transition into the 10–18-in. layer corresponding to the A_2 horizon, which is lighter-coloured and shows the highest concentration of quartz gravel (see Table 1). The 18–36-in. layer may represent an incipient B horizon at a very early stage of development. The presence of scattered small fragments of feldspar and minute flakes of muscovite indicates a close genetic relationship to the underlying C horizon. On the other hand this layer differs from the rest of the profile in its tendency to form subangular blocky peds and its orange colour. There is also a sharp rise in the content of clay and a reduction in quartz gravel when compared with the overlying A_2 horizon.

The two bottom layers constitute the C horizon, in which the clay content is much higher than in the upper part of the profile.

Buwekula Red. This series occurs on the upper middle and middle slopes of hills and is the most extensive member of the catena. If the concept of soil zonality were applied to the present soil sequence, Buwekula Red would be regarded as the 'normal soil' having its features in equilibrium with its present environment (U.S.D.A., 1951). The profile is as follows:

0–3″ Dark brown (7·5 YR 4/2) humose sandy loam+occasional quartz gravel. Frequent roots. Weakly crumbly and firm.

3–8″ Red-brown (5 YR 4/3) less humose, sandy clay-loam+frequent quartz gravel. Frequent roots. Weakly granular and slightly compact.

8–18″ Yellow-red (5 YR 4/6) slightly stained with humus, sandy clay-loam+

* All the Munsell colour determinations were made on air-dry soil samples.

frequent quartz gravel+occasional quartz stones. Weakly granular and slightly compact.

18–40″ Red (2·5 YR 5/8) sandy clay-loam+frequent humose streaks+frequent quartz gravel+occasional quartz stones+occasional, semi-rounded hard ironstone concretions ($\frac{1}{2}$–$1\frac{1}{2}$ cm.). Slightly compact. Breaks into subangular blocks of varying size.

40–60″ Red (2·5 YR 5/8) sandy clay-loam+faint humose streaks+frequent quartz gravel and stones+occasional grey, yellow, and red mottles+occasional dull brown and irregular ironstone concretions. Structureless and compact.

60–72″ Red (2·5 YR 5/8) strongly mottled grey, red, and yellow clay-loam+occasional soft ferruginous specks. Structureless and very compact.

The last whole depth of the horizon is several feet and gradually merges into loose, friable, and gritty rotten rock.

The A_1 horizon consists of two layers, 0–3 in. and 3–8 in., and is followed by the transitional 8–18-in. layer which merges into a weakly developed B horizon between 18 and 40 in. Concretions in this horizon are dark brown and semi-rounded. The 40–60-in. layer represents another transition into the mottled and slightly indurated horizon which appears to be enriched with iron compounds forming a discontinuous ferruginous network. Concretions in the 40–60-in. layer are irregular in shape and of dull brown colour closely resembling cemented clay fragments.

The middle layers of Buwekula Red may be irregularly streaked with dark humose material. This may be due to the action of soil fauna, or inwashed clay from the upper soil layers.

Buwekula Brown. This series occurs on the low middle and lower slopes and is generally far less extensive than Buwekula Red. It may be regarded as a topohydric variant of Buwekula Red which has been altered by drainage as influenced by topography. The profile is described as follows:

0–3″ Grey-brown (10 YR 5/2) humose sandy loam+frequent fine quartz gravel. Frequent roots. Weakly crumbly and loose.

3–8″ Red-brown (5 YR 5/3) less humose gravelly loam+occasional small quartz stones. Weakly granular to structureless. Frequent roots.

8–20″ Red-brown (5 YR 5/3) slightly stained with humus, gravelly loam+frequent coarse gravel and quartz stones. Weakly granular to structureless.

20–36″ Yellow-red (5 YR 5/6) gravelly clay-loam+frequent dark brown streaks+frequent coarse gravel and occasional stones+occasional ironstone concretions. Weak subangular blocky structure. Slightly compact.

36–60″ Yellow-red (5 YR 5/8) gravelly clay-loam+frequent dark yellow, dark grey, and brown mottles+some irregular ironstone concretions. Structureless and compact.

60–72″ Reddish-yellow (7·5 YR 6/8) indurated material, strongly mottled dark yellow, dark grey, and brown+occasional semi-hard ferruginous specks. Very compact and structureless.

The arrangement of the main horizons in this series is very similar to that of its red associate. The light-textured A horizon, including a transitional zone, extends to 20 in. and is underlain by the colour B horizon from 20 to 36 in. The transition ir to the mottled horizon begins at 36 in. and the latter occurs from 60 in. downwards.

Although the main morphological features are the same in both of these series, Buwekula Brown shows the following differentiating characteristics in addition to its brown colour. The first three layers have a much lower clay content associated with a considerable increase in quartz gravel which may account for partial eradication of structural features. The mottles found in the lower horizons lack the bright colours of Buwekula Red and there is a distinct predominance of yellow, brown, and dark grey indicating an advanced degree of hydration. In the lower horizons the concretions tend to be more numerous though by no means abundant. They are duller and less rounded than those of Buwekula Red.

Buwekula Yellow-Brown. This series occurs on slightly raised valley bottoms and valley slopes, and is described as follows:

0–3″ Grey (10 YR 5/1) humose loamy sand. Weakly crumbly and firm. Frequent roots.
3–8″ Light brownish-grey (10 YR 6/2) less humose loamy sand. Very weak crumb structure. Loose.
8–18″ Pale brown (10 YR 6/3) slightly stained with humus, coarse sand. Structureless and slightly compact.
18–36″ Light yellow-brown (10 YR 6/4) coarse sand, structureless and slightly compact. Sharp change to
36–60″ Very pale brown (10 YR 8/3) mottled rusty brown coarse sand. Structureless and compact.
60–72″ Light grey (10 YR 7/1) loamy sand with occasional rusty brown mottles. Structureless and compact.

The first two layers constitute the A_1 horizon. The underlying layer is transitional and merges into what may be an equivalent of a weakly developed colour B horizon which has been formed from the underlying material as a result of improved drainage conditions. This horizon extends to 36 in. approximately and its lower boundary marks the upper limit of a fluctuating water table in a normal rainy season. With an exceptionally high rainfall this horizon may become waterlogged but only for a very short time. The two bottom layers represent the grey C horizon similar to that occurring in the grey associate. The upper layer displays more frequent and larger rusty brown mottles which indicate longer periods of seasonal aeration due to the water table receding to greater depths in the dry season.

Buwekula Grey. This series occurs on the valley floor a few feet above the level of the stream and is often completely submerged in the rainy season. In larger flat-bottomed valleys such soils are permanently waterlogged and remain under swampy vegetation. The profile description is as follows:

0–3″ Grey (10 YR 5/1) humose loamy sand. Weakly crumbly and firm. Frequent roots.
3–8″ Grey (10 YR 6/1) stained with humus, coarse sand. Structureless and loose.
8–18″ Light grey (10 YR 7/1) slightly stained with humus, coarse sand with frequent rusty brown mottles. Structureless and loose.
18–36″ Light grey (10 YR 7/1) coarse sand with occasional faint rusty brown mottles. Structureless and loose.

frequent quartz gravel+occasional quartz stones. Weakly granular and slightly compact.

18–40″ Red (2·5 YR 5/8) sandy clay-loam+frequent humose streaks+frequent quartz gravel+occasional quartz stones+occasional, semi-rounded hard ironstone concretions (½–1½ cm.). Slightly compact. Breaks into subangular blocks of varying size.

40–60″ Red (2·5 YR 5/8) sandy clay-loam+faint humose streaks+frequent quartz gravel and stones+occasional grey, yellow, and red mottles+occasional dull brown and irregular ironstone concretions. Structureless and compact.

60–72″ Red (2·5 YR 5/8) strongly mottled grey, red, and yellow clay-loam+occasional soft ferruginous specks. Structureless and very compact.

The last whole depth of the horizon is several feet and gradually merges into loose, friable, and gritty rotten rock.

The A_1 horizon consists of two layers, 0–3 in. and 3–8 in., and is followed by the transitional 8–18-in. layer which merges into a weakly developed B horizon between 18 and 40 in. Concretions in this horizon are dark brown and semi-rounded. The 40–60-in. layer represents another transition into the mottled and slightly indurated horizon which appears to be enriched with iron compounds forming a discontinuous ferruginous network. Concretions in the 40–60-in. layer are irregular in shape and of dull brown colour closely resembling cemented clay fragments.

The middle layers of Buwekula Red may be irregularly streaked with dark humose material. This may be due to the action of soil fauna, or inwashed clay from the upper soil layers.

Buwekula Brown. This series occurs on the low middle and lower slopes and is generally far less extensive than Buwekula Red. It may be regarded as a topohydric variant of Buwekula Red which has been altered by drainage as influenced by topography. The profile is described as follows:

0–3″ Grey-brown (10 YR 5/2) humose sandy loam+frequent fine quartz gravel. Frequent roots. Weakly crumbly and loose.

3–8″ Red-brown (5 YR 5/3) less humose gravelly loam+occasional small quartz stones. Weakly granular to structureless. Frequent roots.

8–20″ Red-brown (5 YR 5/3) slightly stained with humus, gravelly loam+frequent coarse gravel and quartz stones. Weakly granular to structureless.

20–36″ Yellow-red (5 YR 5/6) gravelly clay-loam+frequent dark brown streaks+frequent coarse gravel and occasional stones+occasional ironstone concretions. Weak subangular blocky structure. Slightly compact.

36–60″ Yellow-red (5 YR 5/8) gravelly clay-loam+frequent dark yellow, dark grey, and brown mottles+some irregular ironstone concretions. Structureless and compact.

60–72″ Reddish-yellow (7·5 YR 6/8) indurated material, strongly mottled dark yellow, dark grey, and brown+occasional semi-hard ferruginous specks. Very compact and structureless.

The arrangement of the main horizons in this series is very similar to that of its red associate. The light-textured A horizon, including a transitional zone, extends to 20 in. and is underlain by the colour B horizon from 20 to 36 in. The transition into the mottled horizon begins at 36 in. and the latter occurs from 60 in. downwards.

Although the main morphological features are the same in both of these series, Buwekula Brown shows the following differentiating characteristics in addition to its brown colour. The first three layers have a much lower clay content associated with a considerable increase in quartz gravel which may account for partial eradication of structural features. The mottles found in the lower horizons lack the bright colours of Buwekula Red and there is a distinct predominance of yellow, brown, and dark grey indicating an advanced degree of hydration. In the lower horizons the concretions tend to be more numerous though by no means abundant. They are duller and less rounded than those of Buwekula Red.

Buwekula Yellow-Brown. This series occurs on slightly raised valley bottoms and valley slopes, and is described as follows:

0–3″ Grey (10 YR 5/1) humose loamy sand. Weakly crumbly and firm. Frequent roots.
3–8″ Light brownish-grey (10 YR 6/2) less humose loamy sand. Very weak crumb structure. Loose.
8–18″ Pale brown (10 YR 6/3) slightly stained with humus, coarse sand. Structureless and slightly compact.
18–36″ Light yellow-brown (10 YR 6/4) coarse sand, structureless and slightly compact. Sharp change to
36–60″ Very pale brown (10 YR 8/3) mottled rusty brown coarse sand. Structureless and compact.
60–72″ Light grey (10 YR 7/1) loamy sand with occasional rusty brown mottles. Structureless and compact.

The first two layers constitute the A_1 horizon. The underlying layer is transitional and merges into what may be an equivalent of a weakly developed colour B horizon which has been formed from the underlying material as a result of improved drainage conditions. This horizon extends to 36 in. approximately and its lower boundary marks the upper limit of a fluctuating water table in a normal rainy season. With an exceptionally high rainfall this horizon may become waterlogged but only for a very short time. The two bottom layers represent the grey C horizon similar to that occurring in the grey associate. The upper layer displays more frequent and larger rusty brown mottles which indicate longer periods of seasonal aeration due to the water table receding to greater depths in the dry season.

Buwekula Grey. This series occurs on the valley floor a few feet above the level of the stream and is often completely submerged in the rainy season. In larger flat-bottomed valleys such soils are permanently waterlogged and remain under swampy vegetation. The profile description is as follows:

0–3″ Grey (10 YR 5/1) humose loamy sand. Weakly crumbly and firm. Frequent roots.
3–8″ Grey (10 YR 6/1) stained with humus, coarse sand. Structureless and loose.
8–18″ Light grey (10 YR 7/1) slightly stained with humus, coarse sand with frequent rusty brown mottles. Structureless and loose.
18–36″ Light grey (10 YR 7/1) coarse sand with occasional faint rusty brown mottles. Structureless and loose.

The water table occurred at 36 in.

The profile consists of the sandy A_1 horizon about 8 in. in thickness, merging through the transitional 8–18-in. layer into the seasonally waterlogged C horizon. Rusty brown mottles in the grey soil material are evidence of alternate reducing and oxidizing conditions caused by seasonal fluctuations of the water table.

Analytical Results

Mechanical analysis. Stones and gravel were determined by 2-mm. sieving and direct weighing. Silt and clay were measured by the Bouyoucos hydrometer method and sand obtained by difference.

TABLE I

Mechanical Analysis

Horizons (in.)	*Coarse fraction gravel and stones (% whole soil)*	*Fine-earth fraction < 2 mm.*		
		Clay	*Silt*	*Sand*
		(% fine earth)		
Buwekula Shallow				
0–3	44	18	6	76
–10	56	16	2	82
–18	72	7	1	92
–36	51	25	7	68
–60	60	45	8	47
–72	63	41	5	54
Buwekula Red				
0–3	7	29	5	66
–8	11	35	4	61
–18	15	34	2	64
–40	27	47	0	53
–60	11	51	4	45
–72	16	50	2	48
Buwekula Brown				
0–3	10	14	8	78
–8	51	24	2	74
–20	66	24	4	72
–36	44	42	8	50
–60	40	48	4	48
–72	35	54	6	40
Buwekula Yellow-Brown				
0–3	2	9	2	89
–8	13	12	4	84
–18	7	9	6	85
–36	4	7	8	85
–60	1	7	8	85
–72	0·5	11	6	83
Buwekula Grey				
0–3	1	9	8	83
–8	11	7	6	87
–18	3	5	4	91
–36	2	0	12	88

All the three upland soils show a relatively low clay content in the upper layers, increasing with depth. Gravel and stones are most frequent in Buwekula Shallow, particularly in the A_2 horizon of this profile. The gravel fraction in the first three layers of this series consists predominantly of angular quartz fragments. From 36 in. downwards, however, quartz gravel is mixed up with fragments of unweathered feldspar. Feldspar fragments do not occur in the other thoroughly weathered upland associates, in which the coarse fraction consists entirely of quartz.

Buwekula Brown is distinctly lighter in texture than its red associate and contains higher proportions of quartz gravel, indicating a more intensive eluviation. The clay content increases with depth as in Buwekula Red.

Both the upland and the alluvial profiles show a very low silt content —a characteristic shared by many tropical soils, in which rapid and intense weathering seems to result in a more or less direct transformation of feldspars into clay with insignificant proportions of silt being formed. Furthermore, a large proportion of the estimated silt fraction does not consist of true silt particles but of re-aggregated clay particles.

The dominant fraction of the alluvial associates is coarse and fine quartzose sand with very small proportions of other constituents. The low proportion of gravel in the alluvial soils indicates fragmentation during transport.

Chemical analysis. pH values were determined by glass electrode (Cambridge pH meter) on soil samples saturated to a wet paste; the content of available phosphorus (P_2O_5) by the Truog method; organic carbon by the Walkley–Black method; and exchangeable cations by the Lundegårdh flame method on a medium quartz spectrograph using neutral normal ammonium-acetate extracts. The figure for exchangeable hydrogen, estimated by the Schofield para-nitrophenol method, was used in calculating the total exchange capacity and the percentage base saturation.

The pH values reveal that all the members of this catena are acid and characterized by an advanced degree of leaching. The highest pH values are encountered in the A_1 horizon of Buwekula Shallow: pH values of just over 6 were recorded from samples of this layer elsewhere. The acidity increases with depth in all the profiles except in Buwekula Red where there is a slight rise in pH in the lower layers. With low percentages of base saturation both Buwekula Red and Buwekula Brown may be regarded as through-leached soils. The main factor responsible for their present pH trend appears to be rainfall.

X-ray analysis of the clay was not carried out, but the total exchange capacities of these soils seem to be typical of a clay complex consisting of kaolinite. The exchangeable bases show a remarkably high proportion of magnesium to calcium—a phenomenon also observed in Tanganyika (Muir *et al.*, 1957) and there attributed to a hornblendic parent rock. There is no hornblende in the parent rock of Buwekula soils which are derived from quartzose granites, and the high content of exchangeable magnesium may perhaps be due to differential leaching with calcium and

potassium being lost at a more rapid rate than magnesium (de Endredy and Montgomery, 1956).

TABLE 2

Chemical Analysis

Horizons (in.)	*pH*	P_2O_5 *(p.p.m.)*	*C (%)*	*Exchangeable cations (m.e./100 g.)*				*Total exchange capacity (m.e./100 g.)*	*Base saturation (%)*
				Ca	*Mg*	*K*	*Mn*		
Buwekula Shallow									
0–3	5·8	12	2·13	3·0	1·8	0·31	<0·02	10·9	46·9
–10	5·7	13	2·12	2·3	1·4	0	0	8·6	43·0
–18	5·7	8	0·50	<0·8	<0·6	0	0	3·3	42·4
–36	4·9	9	0·36	<0·8	<0·6	0	0	5·2	26·9
–60	5·0	5	0·14	1·6	1·4	0	0	6·7	44·8
–72	4·9	5	0·08	1·1	1·5	0·25	0	6·8	41·6
Buwekula Red									
0–3	5·6	14	2·01	2·3	1·9	0·66	0·02	10·5	46·6
–8	5·1	10	1·23	2·2	1·1	0·46	0·02	9·8	37·9
–18	4·9	9	0·72	1·4	0·6	0·36	Trace	8·4	28·2
–40	5·2	8	0·39	1·2	1·8	Trace	0	8·0	37·5
–60	5·4	5	0·38	1·2	1·8	Trace	Trace	7·4	40·5
–72	5·9	6	0·15	1·1	1·5	0	0	7·0	37·1
Buwekula Brown									
0–3	5·6	15	1·89	2·0	1·3	0·33	0·04	8·8	41·8
–8	4·9	11	1·29	<0·8	<0·6	0·36	0·03	8·6	20·8
–20	4·9	9	0·78	0	0	0	0	6·8	..
–36	5·0	12	0·33	Trace	0	0	0	6·8	..
–60	4·9	9	0·24	1·0	0	0	0	7·0	14·3
–72	4·9	9	0·29	1·4	<0·6	0	0	8·6	23·2
Buwekula Yellow-Brown									
0–3	5·4	15	1·46	1·6	1·1	0·30	0·04	6·4	47·2
–8	5·0	7	0·75	0·8	Trace	0	0·03	5·1	16·2
–18	4·8	10	0·45	Trace	0	0	<0·02	..	..
–36	4·7	3	0·26	0	0	0	<0·02	4·2	50·3
–60	4·8	5	0·08	<0·8	0	0	0	2·6	30·8
–72	4·8	8	0·12	0·8	<0·6	0	0	3·0	46·7
Buwekula Grey									
0–3	5·3	19	1·52	0·8	0·6	0·16	0·04	6·7	21·2
–8	5·0	4	0·71	0	0	0	0	3·2	..
–18	5·0	4	0·08	0'	0	0	0	1·6	..
–36	5·0	3	0·03	0	0	0	0	1·2	..

As may be expected, the organic carbon is highest in the surface layers and drops sharply with depth. The exchangeable cations and to a large extent the acid-soluble phosphorus are generally highest in the surface layers, demonstrating once again the repeatedly proved fact that most of the easily available plant nutrients in tropical soils are held by the organic colloids in the humose topsoil.

Mineral analysis

The fine-sand fractions (0·2–0·02 mm.) were retained after mechanical analysis of the soils, and semi-quantitative mineralogical examinations carried out. Mineral separations were done with bromoform and a magnet. It was not necessary to treat the sands to remove iron oxide stains. Feldspar percentages were obtained by counts, but the other figures given in Table 3 are estimates.

Quartz is the dominant mineral in most horizons but feldspar is more abundant in some horizons of Buwekula Shallow. The feldspar is extremely weathered and cloudy with alteration products. The heavy minerals are described as follows:

Opaque minerals. Magnetite varied from rounded to euhedral grains. Ilmenite was fairly common as black, non-magnetic grains. Opaque grains which are red or yellow in reflected light are probably goethite or limonite. These are always rounded and may be secondary grains or concretions.

Zircon occurs in a wide variety of forms from perfect euhedra to well-rounded grains and may be of various colours or colourless. Most are slightly worn grains of a pink/brown colour.

Tourmaline is found as platy grains with pleochroism from pale pink to dark green or opaque.

Epidote is usually found as irregular grains with hackly surface, usually showing signs of alteration. Grains are generally dirty green in colour but are often bleached in patches, and dirty with opaque alteration products. A few less weathered grains retain some crystal form and show typical epidote optical properties.

Muscovite and *Biotite* are present as basal flakes with typical colour and interference figures.

Andalusite occurs as slightly corroded grains with typical red to colourless pleochroism.

Rutile of both red and yellow varieties is found as rounded grains.

Apatite is in the form of corroded rounded laths with pitted surface.

Sphene is present as small, yellow/brown diamond-shaped grains with incomplete extinction.

Fig. 5 shows the appearance of some typical heavy minerals.

The relative proportions of minerals are shown in Table 3, and from them certain deductions can be drawn regarding the pedogenesis of both the individual profiles and the catena as a whole.

The most striking feature of this is that Buwekula Shallow is richer than the other profiles in abundance of mineral species, with high proportions of feldspar and magnetite, and having epidote, muscovite, and biotite as main heavy minerals.

These mineralogical features would suggest that Buwekula Shallow had a different parent material than the other upland soils of the catena, the former having a varied mineral assemblage and the latter a poor one. But the geological evidence indicates that both are derived from granite. The solution to this problem lies in the fact that the soils are not derived directly from granite but from weathered granite residue left after a

former cycle of weathering. Buwekula Shallow is formed on fresh or only slightly pre-weathered granite, whereas Buwekula Brown and Red are formed on the residue left after prolonged earlier weathering. The mineralogical evidence for a former cycle of weathering is thus in agreement with the postulated geomorphic history of the area.

FIG. 5.

The minerals present in the alluvial associates show that the alluvium was derived locally, and the scarcity of weatherable heavy minerals indicates that the pre-weathered rock, rather than fresh rock, made the largest contribution. The abundance of opaque heavy minerals other than magnetite is due to alluvial concentration of ilmenite, and has no pedological significance.

Magnetite shows rather surprising weatherability, being present in quite large amounts in Buwekula Shallow, but in small quantities in the other associates.

Zircon and tourmaline, two extremely resistant minerals, persist throughout the catena in all series and all horizons.

To summarize, the mineralogical evidence indicates that there were three parent materials concerned in the formation of the Buwekula catena. Buwekula Shallow is derived from fresh or slightly pre-weathered granite, Buwekula Red and Brown are derived from intensely pre-weathered granite, and Buwekula Yellow-Brown and Grey are formed on alluvium derived from pre-weathered granite.

When each soil series is considered in turn, there is some mineralogical evidence for weathering within the profile, that is pedological weathering in the present cycle.

In all profiles except Buwekula Grey there is depletion of feldspar towards the top of the profile. This is well marked in Buwekula Shallow; Buwekula Red, having very little feldspar anyway, does not show this so well. The deep subsoil of Buwekula Red and Brown also show depletion, but the significance of this is not known. Buwekula Grey provides no

TABLE 3

Mineral Analysis

Depth (in.)	*Relative amount of heavy minerals*	*% magnetite in heavy fraction*	*% other opaque minerals after removal of magnetite*	*% feldspar in light fraction*	*Main non-opaque heavy minerals*	*Accessory non-opaque heavy minerals*
Buwekula Shallow						
0–3	2	50	50	56	Z, T, E	M
–10	2	50	40	45	Z, T, E, M	..
–18	5	20	50	75	Z, T, E, M	..
–36	3	50	70	72	Z, T, E, M, B	R
–60	5	40	70	70	Z, T, E, M, B	R
–72	5	60	60	75	Z, T, E, M, B	
Buwekula Red						
0–3	10	5	50	0	Z, T	M, E, R
–8	5	5	50	0	Z, T	M
–18	5	10	50	1	Z, T	A, E
–40	5	10	50	1	Z, T	E
–60	3	20	50	1	Z, T	M
–72	6	10	90	0	Z, T	M
Buwekula Brown						
0–3	50	5	30	0	Z, T	M, At, S
–8	50	5	30	0	Z, T	M, At, S
–20	5	5	30	6	Z, T	A, E
–36	3	5	80	10	Z, T	R, A
–60	2	5	70	6	Z, T	A
–72	6	3	60	1	Z, T	M
Buwekula Yellow-Brown						
0–3	3	5	60	5	Z, T	R
–8	4	10	80	4	Z, T	A, M
–18	3	3	80	5	Z, T	A, E
–36	2	3	80	12	Z, T	M
–60	1	3	80	10	Z, T	A, M
–72	4	20	70	14	Z, T	A, R
Buwekula Grey						
0–3	2	1	80	10	Z, T	R
–8	1	0	90	12	Z, T	..
–18	1	0	80	6	Z, T	..

Z, Zircon; T, Tourmaline; E, Epidote; M, Muscovite; B, Biotite; R, Rutile; A, Andalusite; S, Sphene; At, Anatase.

mineralogical evidence for weathering *in situ*, presumably because there has been insufficient time for appreciable weathering since deposition.

Magnetite provides similar evidence of weathering within the profile in some cases. Removal of feldspar by weathering should cause a corresponding increase in the relative amount of heavy minerals if the

latter are not weathered. This increase is very marked in Buwekula Red and Brown. Buwekula Shallow does not show this trend because some of the heavy minerals are weathered out at the same time.

Buwekula Shallow demonstrates a very nice sequence of weathering in the non-opaque heavy minerals. Biotite is the first mineral to go, and then muscovite. Epidote persists to the surface but would be the next mineral to go, and is absent in the more weathered associates.

The mineralogical evidence shows plainly that the soils are sedentary and not transported. Drift from the fresh rock on to Buwekula Shallow would increase the proportion of weatherable minerals in the upper layers. In fact there is a decrease in weatherable minerals in the topsoil. Drift from Buwekula Shallow on to Buwekula Red or Brown would contain a high proportion of feldspar. In fact there is no feldspar in the topsoils of Buwekula Red and Brown.

Minor heavy minerals show little of importance except that muscovite and epidote, common in Buwekula Shallow, occur as occasional grains in many of the other soils.

Pedology

From the field and laboratory data presented it is possible to come to several conclusions regarding the origin of the soils and the processes which gave rise to them. Each component of the Buwekula catena will now be discussed in turn.

Buwekula Shallow. The most important factor in the pedogenesis of this profile is the nature of the parent material. In the light of its geomorphic setting it seems probable that the parent material was only slightly weathered rock situated in the zone just above the basal surface of weathering in a previous cycle. This has subsequently been exposed by erosion to the present land surface and the present cycle of weathering has caused further changes. This second weathering is reflected in the mineralogical analyses.

Due to its closeness to the basal surface of weathering Buwekula Shallow usually occurs in the vicinity of rock outcrops often on hilltops and upper slopes. The bare rocks contain many cracks and fissures and act as water-collecting surfaces. Rainwater penetrates the rocks and often emerges at their bases in the form of springs. The soils immediately below are thus subjected to rapid lateral drainage and consequent eluviation. This accounts for a high content of residual quartz gravel in the upper horizons of Buwekula Shallow.

Buwekula Red. This soil differs from Buwekula Shallow in the degree of weathering, which can be explained by a considerable difference in the type of parent material. The parent rock is no longer a limiting factor in the formation of Buwekula Red, where an almost complete decomposition of primary minerals, mobilization of iron, and the formation of the mottled and semi-indurated horizon indicate prolonged and thorough weathering. The iron concretions in the 40–60-in. layer are irregular in shape and of dull brown colour, closely resembling cemented clay fragments. In the 18–40-in. horizon they become darker brown, somewhat polished, and semi-rounded. This

progressive change in shape and appearance of the concretions has been observed in other parts of the tropics, particularly West Africa (Vine, 1949; Nye, 1955). Nye recognizes a range of maturity in such concretions and suggests that their formation and subsequent destruction is a contemporary process. This is quite evident in Buwekula Red though the intensity of this process is much lower than in some other soils, most likely due to a low content of ferromagnesian minerals in the parent granite and the consequent limited supply of iron.

With the present arrangement and appearance of the soil horizons in Buwekula Red its genesis may now be postulated. A thorough decomposition to a considerable depth appears to have taken place in a previous cycle of weathering. After a period of erosion formed the present valleys, pre-weathered rock remained on the mid-slopes. In the present cycle there are further changes which are truly pedological.

Intense leaching is reflected in low pH values throughout the solum.* The loss of clay by eluviation from the upper part of the profile induces a condition of relatively rapid internal drainage there whilst the underlying clayey layers are only slowly permeable. Due to the steepness of slopes downslope movement of water is just as important as down-profile movement. This prevents the formation of a true perched water table above the slowly permeable horizon although the latter becomes completely saturated in the wet season. Therefore, the precipitation of iron in the lower part of the profile and the consequent formation of the mottled and semi-indurated horizon takes place seasonally under alternate wetting and drying conditions.

Although there is no mineralogical evidence for hill creep, it is quite evident that on such steep slopes and under such a rainfall there must be some downslope eluviation of the finer soil fraction at least and the mechanical analyses support this. As indicated by a high content of quartz sand in the alluvial associates the upper eluviated horizons of Buwekula Red must be gradually removed by erosion enabling rainwater to penetrate more effectively into the lower horizons which are subjected to the same process of clay eluviation. However, the process of iron movement and its precipitation is taking place all the time and although the mottled subsoil seems to be gradually destroyed from above, it may develop downwards by encroaching on the underlying deeply weathered soil substratum. Under natural conditions the mottled subsoil is never exposed to the surface but always follows the slope gradient, at a certain depth.

The iron concretions formed at depth are never found in the surface layers of this soil and it is possible that with the lowering of the A_1 horizon they are redissolved, most likely under the influence of organic compounds derived from humus (Bremner *et al.*, 1946; Bloomfield, 1954).

It may, therefore, be suggested that the profile is in equilibrium with the present environment and that the development of all its horizons is keeping pace with all the processes responsible for their removal. In

* Other samples of Buwekula Red show even greater acidity, with pH of the top-soil often below 5.

other words the profile is lowered as a whole and its morphology is not affected.

Buwekula Brown. This series differs from Buwekula Red in texture and colour. A higher content of quartz gravel in its upper layers indicates a more intensive process of clay eluviation. The change of colour from red to brown and the associated dull coloured mottles in the indurated horizon are not caused by impedence of drainage such as occurs in waterlogged depressions. Ground water is moving laterally at much the same rate as that in Buwekula Red, but owing to the lower topographic site a lot more water supplied from higher hill sites passes through this profile. This process is repeated every rainy season and as a result of it the lower horizons of Buwekula Brown remain moist longer after the rains than those of the higher situated soils, though the upper light textured part of the profile is drained rather quickly. Partial hydration of the iron compounds is, therefore, a more lasting process in Buwekula Brown.

Buwekula Brown tends to develop more iron concretions than Buwekula Red. The difference in amount is not great but nevertheless significant, and it may be explained by lateral movement of iron solutions and their precipitation in the lower catenary sites (Greene, 1947).

Despite the differences in profile morphology described above, Buwekula Brown is very similar to Buwekula Red in the arrangement of its main horizons and parent material, suggesting a common genesis. This series originated in the same way as Buwekula Red but on a lower topographic site. Owing to its low position on the pediment Buwekula Brown is subject to excessive lateral run-off which originates on higher parts of the hill and causes considerable eluviation.

The alluvial associates. As shown in Fig. 3 colluvial or hillwash deposits found in other catenas are virtually absent here. This is due to a relatively steep relief under which the erosion products are washed out or moved by creep straight on to the valley bottom. Subsequently they are carried away by running water in the rainy season, during which the activities of streams and rivers rise out of proportion to their sluggish movement in the dry season. As a result of these erosional processes Buwekula Brown passes abruptly into the alluvial soils of valley slopes and bottoms.

The two valley series, though originally derived from weathering and erosion of similar granitic rocks, represent a separate genetic group of soils closely related to each other. Both these series have developed from alluvial deposits which are distinguished by their relative age as reflected by their present topographic position. Buwekula Yellow-Brown was originally formed in the valley bottom where the grey associate now occurs. Owing to subsequent downward cutting of the stream the upper layers of the grey associate emerged beyond the reach of the ground water. The resulting improved drainage conditions and aeration have caused the change of colour from grey to yellow-brown in the upper soil layers and the formation of what may be referred to as the colour B horizon between 18 and 36 in. Although this horizon shows no signs of clay illuviation—due to extremely low clay content in the

profile—and no structure, it differs in colour from both the A_1 and the C horizons. Furthermore, it is derived from the C horizon by improved drainage and aeration.

The C horizon proper, which occurs from 18 in. downwards in Buwekula Grey and from 60 in. downwards in Buwekula Yellow-Brown, is identical in both series. By virtue of its grey colour, induced by intense reduction resulting from more or less permanently impeded drainage conditions, this horizon remains under the influence of the gleying process and may be termed the gleyed C horizon. The term 'gleying' is used here in a wider sense and refers to 'a specific set of soil-water characteristics' (Clarke, 1941, p. 61), rather than to the horizon definition. In the alluvial associates the gleying process affects the parent mâterial represented by the C horizon, but with the subsequent evolution of the soil profile and its transformation from Buwekula Grey into Buwekula Yellow-Brown the intensity of gleying is gradually reduced until it becomes of little or no importance in the B horizon of Buwekula Yellow-Brown.

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REFERENCES

Bloomfield, C. 1954. A study of podzolization. Part III. J. Soil Sci. **5**, 50–56.

Bremner, J. M., Mann, P. J. G., Heintze, S. G., and Lees, H. 1946. Metallo-organic complexes in soil. Nature, **158**, 790–1.

Clarke, G. R. 1941. The Study of the Soil in the Field. 3rd ed. Oxford University Press, London.

de Endredy, A. S., and Montgomery, C. W. 1956. Some aspects of cation exchange in Gold Coast forest soils. Paper submitted to the Sixth Int. Cong. Soil. Sci., Paris.

Greene, H. 1947. Soil formation and water movement in the tropics. Soils and Fertilizers, **10**, 253–6.

Linton, D. L. 1955. The problem of tors. Geog. J. **121**, 470–86.

Milne, G. 1935. Composite units for the mapping of complex soil associations. Trans. Third Int. Cong. Soil Sci. **1**, 345–7.

—— *et al.* 1936. A Provisional Soil Map of East Africa. Crown Agents, London.

Muir, A., Anderson, B., and Stephen, I. 1957. Characteristics of some Tanganyika soils. J. Soil Sci. **8**, 1–18.

Nye, P. H. 1955. Some soil-forming processes in the humid tropics. Part II. J. Soil Sci. **6**, 51–62.

Pallister, J. W. 1956. Slope development in Buganda. Geog. J. **122**, 80–87.

Ruxton, B. P., and Berry, L. The basal rock surface on weathered granitic rocks. (In the Press.)

United States Department of Agriculture. 1951. Soil Survey Manual. Handbook No. 18. Washington, D.C.

VINE, H. 1949. Nigerian soils in relation to parent materials. Comm. Bur. Soil Sci. Tech. Commun. No. 46, pp. 22–29.

WATERS, R. S. 1957. Differential weathering and erosion on old-lands. Geog. J. **123**, 503–9.

WAYLAND, E. J. 1921. Some features of the drainage of Uganda. Geol. Survey Uganda Ann. Rept. for 1920.

—— 1934. Peneplains and some other erosional platforms. Geol. Survey Uganda Ann. Rept. for 1933.

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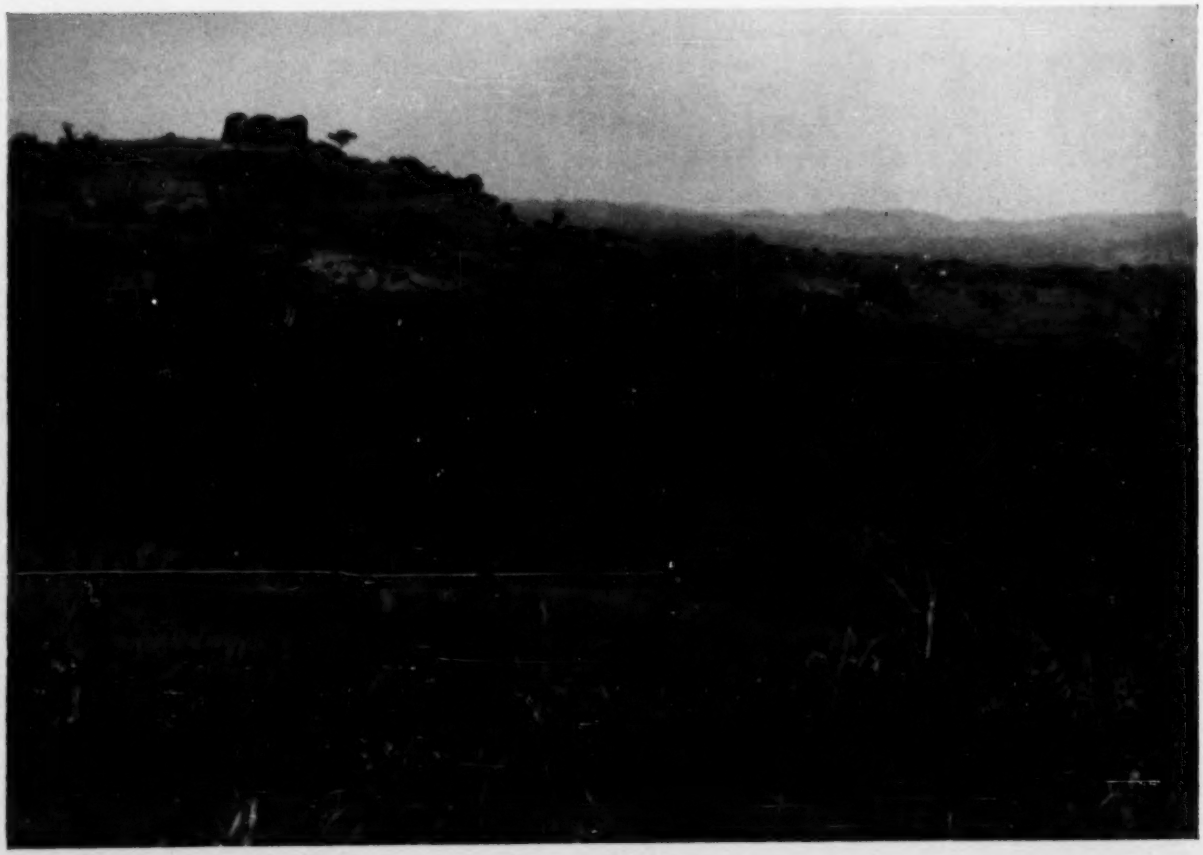

General appearance of the country.
S. A. RADWANSKI *and* C. D. OLLIER—PLATE I

A sharp junction between fresh and weathered rock 'Basal surface of weathering'.

S. A. RADWANSKI *and* C. D. OLLIER—PLATE II

GENERALIZATIONS ON SOME TANGANYIKA SOIL DATA

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Summary

Data on a number of Tanganyika soils are studied in regard to their origins and fertility improvement. Significant differences are shown between the various groups of soils and their clay type is deduced. Cation saturation adjustment—or the controlled addition of Ca, Mg, and K to give saturations for the particular colloid complex optimal for plant growth—is put forward as a new and practicable means of markedly and permanently improving the fertility of highly leached tropical soils.

In 1955 G. H. Gethin Jones and R. M. Scott, of the East African Agricultural and Forestry Research Organization, made a tour of approximately the eastern half of Tanganyika and collected samples from 105 soil profiles. These were analysed in the laboratories of E.A.A.F.R.O. by M. T. Friend and the results, presenting the largest body of strictly comparable soil data ever assembled on Tanganyika soils, were sent to me by G. H. Gethin Jones. An attempt is here made to extract general information from these data, and permission to use them, given by the Director, E.A.A.F.R.O., is gratefully acknowledged.

Classification of the Soils

A uniform soil classification for East Africa—Kenya, Uganda, Tanganyika, and Zanzibar—is still not agreed and in fact much field work remains to be done, but on the basis of past studies (Milne, 1936, Calton, 1954, Gethin Jones and Scott, 1956, and Government Chemist, 1956) it is possible to arrange most of the soils collected by Gethin Jones and Scott under headings which connote recognizable field entities and which will be generally understood.

These are:

Alluvial soils;	Reddish sands;
Red earths;	Yellowish to greyish sands with iron concretions;
Yellowish brown earths;	Plains soils;
Volcanic ash soils;	Cracking clays and sandy clays.

Milne (1936) considered that only 'living alluvium', that is, continually renewed alluvium, like the 'warp' soils of Yorkshire, should be called alluvial, but the definition has proved too strict and as used here the term refers to essentially young soils, generally with fresh minerals, brought into being largely by past river action and now reasonably through-draining. Red earths fit Milne's 'non-laterized red earths', but in modern opinion they are essentially kaolinite soils (Calton, Tidbury, and Walker, 1955; Muir, Anderson, and Stephen, 1957). They are generally deep featureless red soils but they can change rapidly in drainage hollows to black soils with rather plastic clay. Red earths are considered much more mature than the alluvial soils. Yellowish brown earths fit

Milne's 'laterized red earths' and these generally occupy areas with higher rainfall than the red earths. It is assumed that they represent a further stage in soil evolution. Volcanic-ash soils were recognized by Milne, but later work, in particular by Spurr (1954 and 1955), has shown rather complex soil conditions, extensive areas of shallow ash overlying older soils of different derivation and some pumice-layered soils (Government Chemist, 1954 and 1956). They are quoted together because their topsoils have similar characteristics. These volcanic-ash soils centre around Mt. Rungwe in South Tanganyika and are generally subject to heavy rainfall and are thus different from the ash soils found under drier conditions in other parts of the territory. Reddish sands do not form a very distinct pedological group. They are probably best considered as red-earth types influenced by parent-material peculiarity —marked sandiness. Yellowish to greyish sands with iron concretions are usually catenary associates of the reddish sands. Plains soils are the least understood of the soils groups mentioned, but it seems that they represent illuvial or static types not associated with wet conditions. Cracking clays and sandy clays generally fit the fairly well known group of tropical black earths.

Differences in Composition of the Soils

A general appreciation of the differences between these groups of soils can be got by comparing the mean values of the constituents determined (Table 1). Topsoils and lower subsoils only are given and the latter, sampled at about 30–40 inches, is taken to indicate the basic character of the profile, largely uninfluenced by variable topsoil organic matter. In some of the groups with illuvial tendencies, however, the lower subsoil will not truly reflect topsoil less organic matter.

(*a*) *Physical.* In mechanical composition the alluvial soils show a higher clay content in the topsoil than the subsoil. This could be due to variation in the parent alluvium, but it is also possible that there is more weathering of fresh minerals to clay in the upper than in the lower layers. Such a condition has been demonstrated (Government Chemist, 1955) in an old alluvium of uniform silty character containing mica fragments. The red earths, yellowish brown earths, and the reddish sands show washing-down of clay. The volcanic-ash soils might appear to show this also, but the subsoils may be of different derivation from the topsoils and the silt figures are discordant. The mechanical composition of the greyish sands is probably best explained as the result of washing-out of clay. Iron concentrations generally occur and indicate a fluctuating high watertable. Plains soils and cracking clays show marked uniformity in their texture profile. It has been suggested (Vageler, 1933) that in the latter group textural uniformity arises from the mixing which could occur from soil particles falling down deep cracks. It would seem quite as plausible that these soils have been laid down by steady colluvial/alluvial action and that uniformity is maintained in the absence of marked through leaching.

pH data are generally unremarkable. They are high in the plains soils and the cracking clays as would be expected from the high cation

saturation. The most leached soils—yellowish brown earths and reddish sands—show the lowest pH's but are not as low as would be found in podzol horizons or unsaturated clays of the montmorillonite class.

TABLE 1

Mean Composition of Topsoils and Lower Subsoils

(1 = topsoil; 2 = lower subsoil)

		Coarse sand	*Fine sand*	*Silt*	*Clay*	*pH*	*Org. C*	*C/N*	*Exch. Ca*	*Mg*	*K*	*Total*	*Cation exchange capacity*
Alluvial soils	1	18	29	17	33	6·1	2·8	16·2	13·9	7·5	1·28	22·9	28·1
(6 profiles)	2	41	24	14	20	6·1	0·5	10·4	7·5	3·3	0·77	11·9	15·6
Red earths	1	30	30	12	23	6·0	2·6	14·7	5·9	2·8	1·30	10·1	15·7
(18 profiles)	2	23	27	15	34	5·8	0·5	10·9	3·0	2·0	1·11	6·2	10·7
Yellowish brown earths	1	24	34	10	26	5·4	3·4	15·5	2·3	1·3	0·81	4·5	12·6
(5 profiles)	2	20	31	8	40	5·3	0·8	11·5	0·2	0·1	0·57	1·1	6·3
Volcanic ash soils	1	22	41	8	17	5·8	7·0	14·3	5·5	1·7	0·92	8·1	17·7
(8 profiles)	2	24	30	18	27	5·5	1·0	9·0	1·8	1·3	0·89	4·2	10·2
Reddish sands	1	58	28	6	7	5·8	0·7	12·5	1·1	0·7	0·27	2·2	6·2
(10 profiles)	2	51	25	6	17	5·4	0·3	7·3	0·5	1·0	0·34	2·0	5·6
Greyish sands	1	68	25	4	2	6·2	0·8	15·2	2·2	0·5	0·31	3·0	5·7
(11 profiles)	2	65	25	5	5	5·8	0·3	9·0	1·0	0·3	0·22	1·8	4·7
Plains soils	1	39	27	12	17	7·7	1·0	10·8	7·8	3·0	1·40	13·6	16·7
(5 profiles)	2	39	29	19	12	7·4	0·5	9·7	10·0	4·1	1·93	18·2	19·5
Cracking clays and sandy clay	1	16	25	18	37	7·8	1·7	15·2	28·1	8·2	1·10	43·4	45·3
(6 profiles)	2	15	25	19	38	7·5	1·7	17·1	27·2	9·0	0·71	41·7	43·4

(*Note:* The range of variation of each constituent within the groups, omitted for clarity, is rather wide. Average values, which in many cases reflect modal values, are regarded as sufficiently reliable for the purposes of this discussion).

(*b*) *Chemical.* Organic-carbon figures show a marked build-up of organic matter in the volcanic-ash topsoils, that is humifying adequately and is not peaty. Milne (unpublished report) found, some time ago, that these soils had a remarkable capacity for absorbing moisture and attributed this to a micro-vesicular structure of the coarser soil particles. It is probably this factor of very high moisture retention which is responsible for organic-matter build-up. The cracking clays show no diminution of organic carbon and an increase in C/N ratio with depth. This would support the suggestion that these soils are mainly of lateral origin, but the data are insufficient to conclude that cracking clays generally have this type of organic-matter profile.

Apart from the cracking clays, C/N ratio generally decreases with depth, and the most likely explanation of this is that if a C/N ratio of 10 can be taken as normal the topsoils contain some not completely humified material.

The exchangeable-cation data show a number of expected features.

The sands are quite low in cations whereas the plains soils and cracking clays have considerable to quite high amounts. There is a steady decline in exchangeable Ca and Mg from the young alluvial soils to the red earths and then to the yellowish brown earths.

The exchangeable-cation status is of considerable importance both in regard to soil origins and present fertility, and cation proportions are presented in Table 2. But before discussing these it is of some interest to try to work out the contribution of organic matter and of clay to cation-exchange capacity.

TABLE 2

Exchangeable Cations as Percentage Exchange Capacity

(1 = topsoil; 2 = lower subsoil)

		Ca	*Mg*	*K*	*C.E.C.*	% *saturation*
Alluvial soils	1	48	25	5	28·1	78
	2	47	19	6	15·6	72
Red earths	1	34	16	8	15·7	58
	2	21	16	10	10·7	47
Yellowish brown earths	1	17	10	6	12·6	33
	2	4	2	8	6·3	14
Cracking clays	1	62	18	2	45·3	82
	2	62	20	2	43·4	84
Volcanic ash soil	1	31	10	5	17·7	46
	2	18	13	9	10·2	40
Reddish sands	1	18	11	4	6·2	33
	2	9	18	6	5·6	33
Greyish sands	1	39	9	4	5·7	52
	2	21	6	5	4·7	32
Plains soils	1	47	18	8	16·7	73
	2	51	21	10	19·5	82

Relative Contribution of Clay and Organic Matter to Cation-exchange Capacity.

If cation-exchange capacity is assumed in turn to be entirely due to clay and then to organic carbon (as representing organic matter) and the unit values so got are marked on coordinates, a line joining them represents a range of possible equations relating the exchange capacities of clay and of organic carbon to total exchange capacity. Where lines derived from two soils intersect the equation at the point of intersection mathematically satisfied both soils. This equation is not necessarily true, but becomes nearer the truth the nearer the exchange capacities of the clay and of the organic matter of the two soils are together, with the greater error where these diverge falling on the exchange capacity of the organic matter. Where a group of soils of similar clay and organic matter character are plotted it could be expected that the lines will converge on a particular point.

Using this device, very tentatively, on the topsoils and lower subsoils

of the groups of soil under discussion there is in the alluvial soils topsoils a group of intersections centring around a point which gives the following equations:

$$\text{C.E.C.} = 0{\cdot}73\ \text{Cl.} + 2{\cdot}0\ \text{C.}$$

(C.E.C. = cation-exchange capacity in m.e./100 g., Cl. = % Clay, C = % Organic C.)

The red earths give intersections between topsoil and lower subsoil of the same profile in nearly all profiles. One could expect differences in organic matter exchange capacity between topsoil and lower subsoil but in fact the intersections are fairly compact and centre around

$$\text{C.E.C.} = 0{\cdot}13\ \text{Cl.} + 4{\cdot}0\ \text{C.}$$

There are some outlying intersections giving values around 0·3–0·5 for clay and this suggests pedological heterogeneity within this grouping.

With the yellowish brown earths the topsoils and subsoils of each profile intersect and these points centre closely around

$$\text{C.E.C.} = 0{\cdot}09\ \text{Cl.} + 3{\cdot}5\ \text{C.}$$

The equations derived from these groups of soils are in accordance with expectations and the exchange capacities of the soil colloids fall within the range of published data (Russell, 1950; Amphlett, 1958) for specific clay minerals and soil organic matter, which show

Kaolinite	0·03–0·15 m.e./g.
Illite	0·10–0·40 ,,
Montmorillonite	0·8–1·50 ,,
Organic matter	0·5–4·8 m.e./g. C.

The use of this mathematical device on the remaining groups of soils is rather more hazardous, but the graphs are suggestive. Clay exchange capacities appear to be rather higher in the volcanic-ash soils than in the red earths and the yellowish brown earths and organic matter though high seems to have a fairly normal exchange capacity. In both the reddish and greyish sands there is a wide scatter of intersections suggesting that exchange capacity of clay may vary from 0·05 to 1·8, which fits reasonably well the known range of clay variation and confirms the impression that they are pedologically variable. Plains soils and cracking clays give intersections, markedly different from those for red earths and yellow brown earths and the clay value, as one would expect, lies in the vicinity of 1·0. But the range of variation confirms that these two groups of soils are not pedologically uniform.

It is clear even if the above equations are only generally correct that in the alluvial-soils topsoils the bulk of the exchange capacity is supplied by the clay fraction whereas in the red earth and yellowish brown earth topsoils the reverse is true, the bulk of the exchange capacity being supplied by organic matter. Organic matter is presumably the less stable cation holder, but unlike the clay it is normally renewable from the top rather than the base of the profile.

Exchangeable Cations in Relation to Soil Type

As to cation proportions, there are fairly steady K percentages whatever the exchange capacity except in the cracking clays. This more or less constant proportion of K is difficult to explain. The lower K in the cracking clays may be associated with raised Ca. The greyish sands compared with the reddish sands also show increased Ca and it is likely that both the greyish sands and the cracking clays are influenced by lateral accessions of cations. Some of the cracking clays in fact contain rather high exchangeable Na. In the alluvial soils, red earths and yellowish brown earths which represent progressive soil evolution Ca and Mg percentages fall, Ca more sharply than Mg, with decreasing exchange capacity. It seems likely that loss of cations leads to the destruction of exchange capacity.

Exchangeable Cations in Relation to Soil Fertility

Mehlich and Coleman (1952), in a review of the relation of type of soil colloid to the mineral nutrition of plants, show that in soils and in experimental clay-sand mixtures there is an optimum ratio of exchangeable cations for plant growth and that this varies with the type of soil colloid. Cation proportions used in the nutrient culture of plants (Hewitt, 1952) are quite different from those, in exchangeable form, found in fertile soils and it is clear the soil colloids have a marked and variable effect on the availability of cations to plants. It would appear that cation proportions in soils are much more important than the absolute amounts of cations unless these are exceptionally low. As little as 1 m.e. Ca per 100 g. soil is in fact a massive quantity compared with the Ca removed in a crop. Mehlich and Coleman (loc. cit.) give 80 per cent. as an optimum Ca saturation for montmorillonite and illite clays and 40 per cent. for kaolinite and organic colloids and suggest that the Ca/Mg ratio should be between 4 and 6 to 1 and that 5 per cent. saturation with K is generally ideal, but may be lower at exchange capacities above 8 m.e. per 100 g. soil.

In the light of this work the Tanganyika soils under review are adequately supplied with K. K deficiency is in fact rare and has only been found so far locally in one crop (Lock, 1957). On probable clay mineralogy all soils are suboptimal in Ca with the possible exception of the greyish-sands topsoils. The most striking cation unbalance is shown by the yellowish brown earths with Ca lacking in their topsoils and Ca and Mg lacking in their lower subsoils. These shortages work out at 15 cwt. CaO per acre/ft. for the topsoil and 39 cwt. CaO and 5 cwt. MgO per acre/2ft. for the subsoil. These amounts are not large and suggest that a quick and largely permanent build up of basic fertility could be achieved by their correction.

Cation-saturation Adjustment

This conclusion appears to throw new light on the question of raising the fertility of highly leached tropical soils and indeed suggests that soil fertilization generally could be made more precise than at present by adjusting plant nutrient cation saturation in the soil to the most

suitable levels for crops rather than adding arbitary amounts of fertilizers. This looks like 'liming', but all plant nutrient cations are involved and the intention is not simply the adjustment of soil reaction. It might be called C.S.A. (cation saturation adjustment). The amounts of cations required need not be large in soils of low exchange capacity but as they would be considerably greater than the amounts of cations removed annually by crops the improvement could be expected to last a reasonable time. The common advice to add organic matter, almost always grown on the same soil, is contra-indicated, except in so far as it supplies N and helps to retain moisture, because it would raise exchange capacity and require the addition of more cations than would otherwise be adequate. However, in soils with clay of low cation-exchange capacity it would obviously not be advisable to allow organic matter to fall to exceptionally low levels.

Practical Application of Cation-saturation Adjustment

Magnesian limestones occur fairly frequently in Tanganyika, and not far distant from the yellowish brown earths which are particularly short of Ca and Mg. These soils are of major importance to the country's agriculture as they comprise the bulk of the soils found in reasonably well-watered regions. The adjustment of their Ca and Mg saturation might, in addition to correcting the known (Government Chemist, 1951 and 1955) shortages of these in crops, improve the availability of soil P and improve soil structure and microbiological activity, and with the latter might go increased available N. However, the adjustment of Ca and Mg to optimum levels is not put forward as a panacea and P and N additions would almost certainly be required at a higher level of cropping and there are also two other difficulties—micro-nutrient shortages and the practical problem of the rather precise application and mixing in of fertilizers under conditions of primitive agriculture.

Micro-nutrient deficiencies—B, Zn—have already been shown (Calton and Vail, 1956; Vail and Calton, 1957) in some areas of this soil type and are there the most critical factors in crop production. It is likely that further investigation will show that these micro-nutrient deficiencies are more extensive than now known and occur in a wider range of crops and it is also possible that other micro-nutrient elements may be found to be in short supply. The correction of micro-nutrient deficiencies, however, is not difficult once they have been diagnosed and the soil can be by-passed and the nutrients supplied direct to the plant by sprays. It now seems likely that micro-nutrient deficiencies—at any rate of the cation elements—could be more or less permanently corrected by adjusting their saturation on the exchange complex to the levels found in productive soils with the same type of colloid. The relation of the anion elements to anion exchange materials in soils is not clear but if it paralleled cation exchange relations there would exist the possibility of fairly permanent and foolproof correction of all micro-nutrient deficiencies.

It seems that the practical problem of the fairly precise application and incorporation of alkaline materials must be faced if these soils are to be improved. The dangers of overdosing with micro-nutrients known to be

deficient are rather acute. It would be essential to base CaO–MgO dosage on detailed soil and fertilizer analyses, and a further safeguard would be to build up Ca and Mg levels gradually in doubtful areas. Perhaps the greatest danger would lie in farmers' enthusiasm and the simple logic that double the dose would double the response.

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REFERENCES

AMPHLETT, C. B. 1958. Ion exchange in clay minerals. Endeavour, **17**, 149–55.

CALTON, W. E. 1954. An experimental pedological map of Tanganyika. Proc. 2nd Inter-African Soils Conf., Leopoldville, pp. 237–40; document No. 11.

—— and VAIL, J. W. 1956. Micro-nutrient problems in Tanganyika. Proc. 6th Int. Congr. Soil Sci., paper IV. 5.

—— TIDBURY, G. E., and WALKER, G. F. 1955. A study of the more important soils of Zanzibar Protectorate. E. Afr. Agric. J., **21**, 53–60.

GETHIN JONES, G. H., and SCOTT, R. M. 1956. Annual Report, pp. 35–43, East African Agriculture and Forestry Research Organization.

GOVERNMENT CHEMIST. 1951. Annual Report, pp. 5–6. Govt. Printer, Dar es Salaam.

—— 1955. Departmental Reports—unpublished.

—— 1956. Atlas of Tanganyika, p. 4. Chief Surveyor, Department of Lands and Surveys, Dar es Salaam.

—— 1956 *a*. Annual Report, p. 4.

HEWITT, E. J. 1952. Sand and water culture methods used in the study of plant nutrition. Tech. Comm. No. 22, Commonw. Bur. Horticulture and Plantation Crops.

LOCK, G. W. 1957. A manurial trial relating to banding disease of sisal. Emp. J. Exp. Agric., **25**, p. 217–28.

MEHLICH, A., and COLEMAN, N. T. 1952. Type of soil colloid and the mineral nutrition of plants. Adv. Agron. **4**, 67–96.

MILNE G. (in collaboration with V. A. BECKLEY, G. H. GETHIN JONES, W. S. MARTIN, G. GRIFFITH, and L. W. RAYMOND). 1936. A provisional soil map of East Africa (with explanatory memoir). Crown Agents for the Colonies, London.

MUIR, A., ANDERSON, B., and STEPHEN. I. 1957. Characteristics of some Tanganyika Soils. J. Soil Sci. **8**, 1–18.

RUSSELL, E. W. 1950. Soil Conditions and Plant Growth, pp. 86 and 276. Longmans Green & Co., London.

SPURR, A. M. M. 1954. A basis of classification of the soils of areas of composite topography in Central Africa, with special reference to the soils of the Southern Highlands of Tanganyika. Proc. 2nd Inter-African Soils Conf., Leopoldville, document 7, section 11 b.

—— 1955. The soils of Mbozi. Tanganyika Geol. Survey Dep., Bull. 24.

VAGELER, P. 1933. An Introduction to Tropical Soils, p. 179. Trans. by H. Greene. Macmillan, London.

VAIL, J. W., and CALTON, W. E. 1957. Dieback of wattle—a boron deficiency. E. Afr. Agric. J., **23**, 100–3.

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THE ORIGIN AND DEVELOPMENT OF BROWN EARTHS ON CLAY-WITH-FLINTS AND COOMBE DEPOSITS

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Summary

Field investigation of the origin and development of three brown-earth (*sol lessivé*) profiles has been supplemented by mechanical and mineralogical analyses and micromorphological studies. Two profiles, representative of the Batcombe and Winchester series, were on Clay-with-flints and the third, of the Charity series, on a Coombe deposit.

Particle-size distribution and petrographic data strongly suggest that all three soils are derived in part from loess. The Charity is interpreted as an autochthonous profile formed in a Head deposit composed of chalky and flinty detritus mixed with loess by solifluxion, whereas the Batcombe and Winchester are two-stage profiles, formed in composite (non-uniform) parent materials resulting from the superficial incorporation of loess with the truncated or redeposited remains of previously weathered horizons with *rotlehm* and/or *braunlehm* fabrics. These Clay-with-flint substrata contain materials derived from Chalk and Eocene beds in varying proportions, weathered in Tertiary or interglacial periods and rearranged by periglacial agencies. Clay-with-flints *sensu stricto*, as represented in the Winchester subsoil, has distinctive physical, mineralogical, and micromorphological characteristics, and appears to have originated by sub-surface solution of the Chalk and illuvial accumulation of clay derived for the most part from overlying deposits.

The land surfaces concerned have probably been subjected to at least one alternation of periglacial and temperate conditions after the addition of loess. Hence the extent to which either profile reflects the influence of the contemporary environment is not readily assessed, but evidence is adduced that the upper horizons of each profile bear the impress of similar pedogenic processes, including eluviation of clay-size material and acidic weathering leading to the accumulation of vermiculite, modified in the Winchester by the effects of erosion and soil creep.

As defined by Robinson (1949), the major group of brown earths or brown forest soils comprises well-drained and moderately well-drained acid mull soils, occurring naturally under deciduous forest, and characterized by brown, friable, sub-surface horizons which are leached of carbonates and show little or no differential eluviation of sesquioxides. This group includes *braunerde* (Kubiëna, 1953) or *sols bruns acides* (Tavernier and Smith, 1957) with A(B)C profiles, chiefly confined to relatively young land surfaces on silicate rocks or their clastic derivatives, together with texturally differentiated profiles conforming in general to *sols lessivés* as defined by Duchaufour (1956). In southern England, certain *sols lessivés* on younger calcareous drifts have clearly developed ABC profiles typical of grey-brown podzolic soils or *parabraunerde* (Tavernier and Smith, 1957; Kubiëna, 1956*a*) but those associated with Clay-with-flints and other high-level deposits normally have thick, intensively weathered subsoils, resembling those of red-yellow podzolic soils, within which no well defined B and C horizons can be identified. In general, on upland surfaces little affected by recent

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denudation, interglacial or Tertiary soil formations with *braunlehm* or *rotlehm* fabrics appear to have been rearranged by periglacial agencies and frequently modified by loessial additions (cf. Perrin, 1956), so giving rise to composite and two-stage profiles, the morphology of which results only in part from transformation by soil-forming processes operative in Holocene times.

In assessing the origin and development of three brown earths of *sol lessivé* character on the Chiltern Hills, field observations have been supplemented by mechanical and mineralogical analyses of the sand- and silt-size fractions to determine the uniformity (or otherwise) of the soil-forming materials, while micromorphological and clay mineral studies have been used to aid the elucidation of translocation and weathering processes affecting the distribution of clay-size material.

Descriptions of the Soils Studied

The three soils, representative of the Batcombe and Winchester series overlying Clay-with-flints and of the Charity series on Coombe deposits, are sited in beechwoods near Hampden, Bucks., with no record of previous cultivation. Brief descriptions of these series, close analogues of which are widespread on the English Chalk, are given by Avery (1958) and the location of the profiles studied in relation to relief, 'solid' geology, and soil pattern is indicated on the accompanying block diagram (Fig. 1).

Batcombe series

This series comprises moderately well drained to imperfectly drained silt loams and loams overlying plateau deposits mapped as 'Clay-with-flints' or as 'Pebbly Clay and Sand' by the Geological Survey. These heterogeneous accumulations, containing angular and rounded flints in varying proportions, irregularly distributed in a more or less clayey matrix, have generally been interpreted as the weathered remains of Upper Chalk, Eocene (mainly Reading Beds) and later sediments, redistributed by local snow or ice-caps during the early part of the Pleistocene period (Sherlock, 1947). According to Wooldridge and Linton (1955), the summit plateaux in the Hampden area represent relics of a Mio-Pliocene peneplain bevelling the Chalk and Eocene beds, so that the associated drift may well have originated in Tertiary times as a mantle of residual or reconstituted detritus which was subsequently rearranged under periglacial conditions. The profile investigated is as follows:

Profile No.: Bu 14.

Location: Hillock Wood, Great Hampden. *Grid Ref.*: SP/832021.
Slope: 1° even. *Altitude*: 775 feet.
Vegetation: Beechwood with some oak and holly; field layer dominated by bramble (*Rubus* spp.), with scattered herbs, notably *Oxalis acetosella* and *Galeobdolon luteum*.
Horizons:

More or less decomposed litter, up to 1 in. thick, followed in places by traces of black, finely granular humus.

0–2 in. Dark grey to greyish brown* (10 YR 3/1–4/2), friable silt loam with

* Munsell colour names are used in profile descriptions.

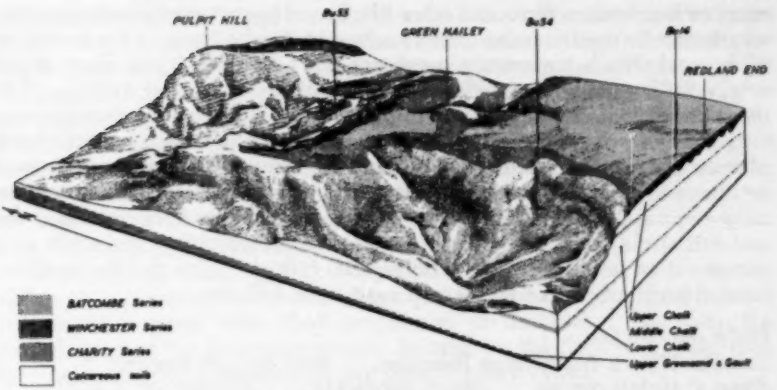


FIG. 1. Location of profiles in relation to relief, geology, and soil pattern.

weak crumb structure; occasional small angular and brown-stained flints; abundant woody roots; earthworms active; clear irregular lower boundary.

2–9 in. Yellowish brown (10 YR 5/6) friable silt loam, pale brown to light yellowish brown when dry, with humose infillings and occasional small flints as above; somewhat compact in place, with very weak crumb structure; frequent woody roots; clear undulating lower boundary.

9–16 in. Strong brown (7·5 YR 5/6), friable to firm, flinty silty clay loam, very faintly mottled with paler and with redder colours; small flints more numerous; fine to medium subangular blocky structure increasingly well defined; aggregate faces have pale-coloured silty coatings particularly evident when dry; occasional small manganiferous concretions; frequent woody roots; clear undulating lower boundary.

16–29 in. Strong brown to yellowish red (7·5 YR–5 YR 5/6), firm flinty silty clay to clay, faintly mottled with light brown and red; flints mainly small and angular; moderate medium to coarse blocky structure; aggregate faces smooth, shiny and paler in colour than interior; common small rounded manganiferous concretions; few roots; merging lower boundary.

29–60 in. Mainly yellowish red, very firm flinty clay, distinctly to prominently mottled with reddish yellow, red, and pale brown to light grey; occasional large, broken and nodular flints with whitish rinds; blocky structure, ill defined in place; consistency variable through mass; greyish material coating flints and lining fissures and root paths is very plastic, while red material is relatively friable; few roots; merging lower boundary.

60–90 in.+ Similar mottled flinty clay, becoming rather more uniform in colour and finer in texture with depth, and containing an increasing proportion of large little-broken flint nodules.

Winchester series

Moderately well drained soils of this series, typically developed on slopes and spurs where plateau deposits thin out, are characterized by subsoil horizons of strong brown to yellowish red, plastic clay, enclosing

more or less broken flints and often blackened by manganiferous deposits, which overlie the irregular Chalk surface at depths from 15 in. to 6 ft. or more, and which apparently represent the Clay-with-flints *sensu stricto* originally regarded as residual from Chalk by Whitaker (1889). The distinctive character of this accumulation, and its widespread occurrence as a lining to the uneven and piped surface of the Chalk beneath both plateau drift and slope deposits of variable lithology, was also recognized by Barrow (1919), who concluded that while the unworn flints it contained were truly residual, being liberated by sub-surface solution, the interstitial clay originated by infiltration from overlying materials in a manner first envisaged by Codrington (1865). The profile studied, located on the brow of the escarpment, is as follows:

Profile No.: Bu 54.

Location: Hillock Wood, Great Hampden. *Grid Ref.*: SP/829027.
Slope: 5° slightly convex. *Aspect*: South-west. *Altitude*: 770 ft. O.D.
Vegetation: Beechwood with some oak; field layer dominated by bramble (*Rubus* spp.) with scattered herbs, notably *Galeobdolon luteum*.
Horizons:

More or less decomposed litter, mainly beech leaves, up to 1 in. thick.

0–2½ in. Very dark grey to greyish brown (10 YR 3/1–4/2), very flinty, friable loam with some bleached sand grains and abundant roots; flints mainly small and angular; occasionally rounded and sub-angular ironstone nodules resembling pisolitic laterite; crumb structure with numerous cavities; earthworms active; clear irregular lower boundary.

2½–7 in. Brown (7·5 YR–10 4/4) very flinty friable loam with humose infillings and abundant roots, grey-brown and soft when dry; shattered flints and ironstone nodules as above; weak crumb structure; clear to sharp and undulating lower boundary.

7–26 in. Yellowish red (5 YR 4/6–5/8) very firm flinty clay with few, faint pale brown and red mottlings and irregular manganiferous deposits which become more prominent with depth; occasional in-filled channels; flints mainly large, more or less broken, nodules; occasional ironstone nodules as above; moderate medium to coarse blocky structure; aggregate faces relatively pale-coloured and locally coated with sand; roots less frequent; this horizon includes patches of relatively flint-free sandy clay loam to sandy clay containing numerous small manganiferous concretions; merging lower boundary.

26–43 in. Yellowish red (5 YR 4/8–5/8) very plastic flinty clay with faint mottling and manganiferous deposits on cleavage faces and flints becoming less evident with depth; flints rather less numerous and largely unbroken; structure weakly expressed in place, but fabric breaks down easily when partly dry to fine blocky aggregates with brown, shiny faces; few roots; sharp irregular lower boundary.

43 in.+ Soft, weathered chalk containing unbroken flint nodules and seams of reddish yellow clay.

Charity series

This series includes well drained, acid, flinty silt loams associated with Coombe (Head) deposits, and typically developed in the Chilterns on even footslopes of 1–5° in the upper and broader parts of the major dip-slope valleys. The underlying deposits, containing shattered flints and

sub-rounded chalk fragments in a loamy calcareous matrix, are sometimes roughly stratified and are interpreted as resulting from the combined agencies of solifluxion and melting snow during a cold phase of the Pleistocene, coeval with either the main Chalky Boulder Clay (Catuvellaunian)* glaciation or an early (Cornovian) phase of the 'Newer Drift' (cf. Oakley, 1936; Arkell, 1947). The watersheds in the wind-gaps have since retreated south-eastwards and the ancient valley floors with their mantle of Head deposits have been dissected by obsequent coombes, probably due to recession of spring heads when the water table was higher than at present (cf. Sparks and Lewis, 1957).

Charity profiles are decalcified to depths of 15 in. to 6 ft. or more, and although variations in the thickness and composition of the horizons sometimes suggest that they originated as successive deposits, the morphology of the following profile, located on the floor of a wind-gap, is consistent with formation *in situ* from Chalky Head.

Profile No.: Bu 55.

Location: Ninn Wood, Monks Risborough. *Grid Ref.*: SP/833040.
Slope: 2° even. *Aspect*: North. *Altitude*: 650 ft. O.D.
Vegetation: Beechwood with ash seedlings in spaces left by felling; field layer, sparse in dense shade, includes *Rubus* spp. and numerous herbs, notably *Asperula odorata*, *Circaea lutetiana*, and *Oxalis acetosella*.
Horizons:

	More or less decomposed litter, mainly beech leaves, up to 1 in. thick.
0–3 in.	Dark grey to greyish brown (10 YR 4/1–4/2), friable flinty silt loam, soft and greyer in colour when dry; flints small and shattered; moderate crumb structure with numerous cavities; abundant woody roots; earthworms present; clear irregular lower boundary.
3–11 in.	Brown (7·5 YR 4/4–5/4) friable flinty silt loam with humose infillings, soft and paler in colour when dry; weak crumb structure; frequent woody roots; clear undulating lower boundary.
11–17 in.	Dark brown (7·5 YR–5 YR 4/4) friable flinty silt loam with weak subangular blocky structure; flints as above; roots less frequent; clear undulating lower boundary.
17–33 in.	Reddish brown (5 YR 4/4) firm flinty silty clay with some black staining and small manganiferous concretions; flints as above, less numerous with depth; moderate medium to coarse blocky structure with waxy colloid-rich coatings and channel fillings; increasingly plastic with depth; horizon 12 to 17 in. thick, with sharp undulating lower boundary.
33 in.+	Pale brown to reddish yellow, very calcareous (33 per cent. $CaCO_3$) silty clay loam with clayey inclusions, containing angular shattered flints and numerous small sub-angular and rounded chalk fragments; compact in place, but friable when dug out.

Methods and Results

Soil samples from each horizon have been used for chemical, mechanical, and mineralogical analyses. Thin sections of selected horizons were

* Charlesworth (1957) equates Arkell's Berrocian and Catuvellaunian glaciations with Mindel (Elster) and Riss (Saale) respectively; Zeuner (1945) adduces a similar correlation. There is, however, no unanimity regarding the correlation of British and continental Pleistocene deposits.

prepared after inpregnation with 'Ceemar Embedding Resin', a polyester resin of low viscosity. Specimens of Upper Chalk and Reading Beds, formations which undoubtedly have contributed to the soils, have also been investigated. The locations of these specimens were as follows:

C 1 Upper Chalk from Hillock Wood, Hampden, Bucks. (*Grid Ref.* SP/828027.)
C 2 Upper Chalk from Whiteleaf Hill, Princes Risborough, Bucks. (*Grid. Ref.* SP/822036.)
RB 1 Reading Beds Lower Clay (Wooldridge and Ewing, 1935) from Lane End, Bucks. (*Grid. Ref.* SU/822917.)
RB 2 Reading Beds (red mottled clay) from Harefield, Middlesex. (*Grid. Ref.* TQ/062883.)
RB 3 Reading Beds (pale coloured clay) from Harefield, Middlesex. (*Grid. Ref.* TQ/062883.)

Non-calcareous residues, prepared from the Chalk samples by treatment with ammonium acetate at pH 3, amounted to $1{\cdot}2 \pm 0{\cdot}1$ per cent. (cf. Jukes-Brown, 1906; Double, 1927): their colour was grey, in sharp contrast to the yellow or yellowish red clay separates from soil horizons.

pH and cation-exchange data (see Table 1)

The surface and sub-surface horizons of all three profiles are strongly acid, and pH values only exceed 5·5 in subsoil horizons of the Winchester and Charity profiles overlying chalky substrata. Both percentage base-saturation and amounts of individual exchangeable cations are at a minimum in sub-surface or upper subsoil horizons, the higher values at the surface being attributable to accumulation of mineral elements derived from the leaf fall. The Ca/Mg ratio is lowest in the Batcombe profile, approaching unity at 36–60 in., while the Winchester and Charity, significantly richer in exchangeable calcium throughout, show minimum values immediately below the surface horizon. In subsoil horizons, of Winchester and Charity profiles in particular, the calculated percentage base-saturation is distinctly higher, relative to pH values, than in upper horizons, suggesting that incomplete displacement of adsorbed ammonium by NaCl may result in low values for cation-exchange capacity.

Particle-size distribution

Mechanical analyses were carried out on the soil samples (< 2 mm.) after dispersion with Calgon, surface horizon samples being pre-treated with H_2O_2. Particles of e.s.d. < 2, 6, and 20μ were determined by the pipette method, while those $> 60\mu$ were separated by sieving; the 60–20μ fraction was obtained by sedimentation or by difference. One-gramme samples of the Chalk residues were similarly analysed.

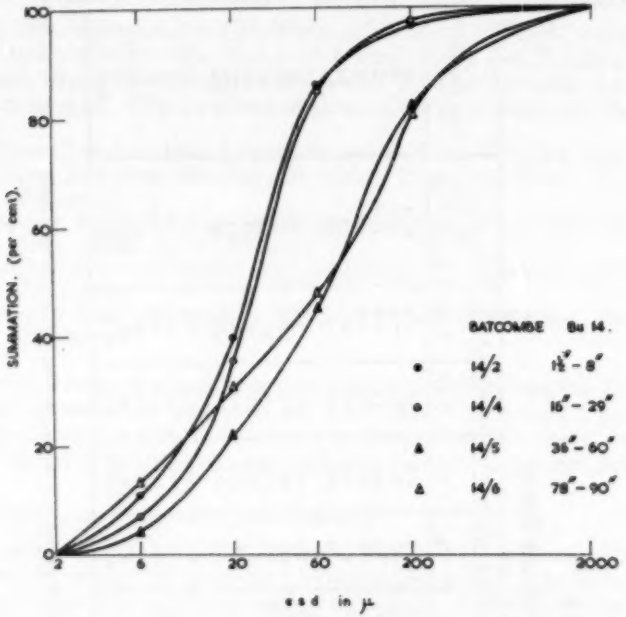
The distribution of six particle-size classes in soils and chalk residues is given in Table 2, and in order to facilitate the identification of similarities in the distribution of sand- and silt-size fractions, the results for selected horizons, recalculated on a clay-free basis, are represented as summation curves in Fig. 2. In interpreting the data, major significance

TABLE I

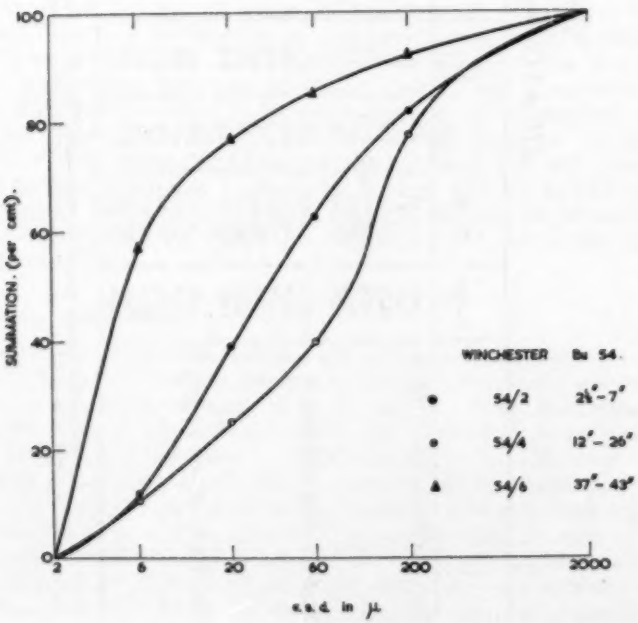
pH and Cation-exchange Data

Soil	*Sample no.*	*Depth (in.)*	*pH*		*•Exchangeable cations (m.e./100 g.)*					*C.E.C.† at pH 7 (m.e./100 g.)*	*'Base saturation' %*
			H_2O	M/100 $CaCl_2$	Ca	Mg	K	Na	*Total*		
Batcombe (flinty) silt loam (Bu 14)	14/1	0–1½	4·4	3·9	1·7	0·4	0·3	Tr.	2·4	16·4	15
	14/2	1½–8	4·5	4·1	0·3	0·1	0·1	Tr.	0·5	8·9	6
	14/3	8–15	4·5	4·1	0·1	Tr.	0·1	Tr.	0·2	10·9	2
	14/4	16–29	4·7	4·1	1·5	0·6	0·1	Tr.	2·2	21	10
	14/5	36–60	5·0	4·0	5·2	4·2	0·2	0·2	10	19	53
	14/6	78–90	4·7	4·0	11	6·9	0·4	0·3	19	31	61
Winchester flinty loam (Bu 54)	54/1	0–2½	4·8	4·4	6·6	0·6	0·3	0·1	7·6	22	35
	54/2	2½–7	4·5	4·0	1·8	0·2	0·1	0·1	2·2	13·8	16
	54/3	7–12	4·3	3·9	10	2·7	0·3	0·2	13	33	41
	54/4	12–25	4·6	4·2	20	4·2	0·4	0·2	25	33	78
	54/5	27–37	5·0	4·5	28	3·6	0·4	0·4	32	43	74
	54/6	37–43	6·4	6·1	45	2·7	0·4	0·3	48	48	100
Charity flinty silt loam (Bu 55)	55/1	0–3	4·6	4·0	5·3	0·7	0·3	0·3	6·6	18	37
	55/2	3–11	4·5	3·8	1·4	0·2	0·1	Tr.	1·7	11·1	15
	55/3	11–17	5·0	4·2	3·8	0·5	0·1	0·1	4·5	11·0	41
	55/4	17–27	5·3	4·7	22	1·3	0·3	0·2	24	27	89
	55/5	27–33	5·8	5·4	25	0·8	0·3	0·2	26	29	90
	55/6	33–39	8·1	7·5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

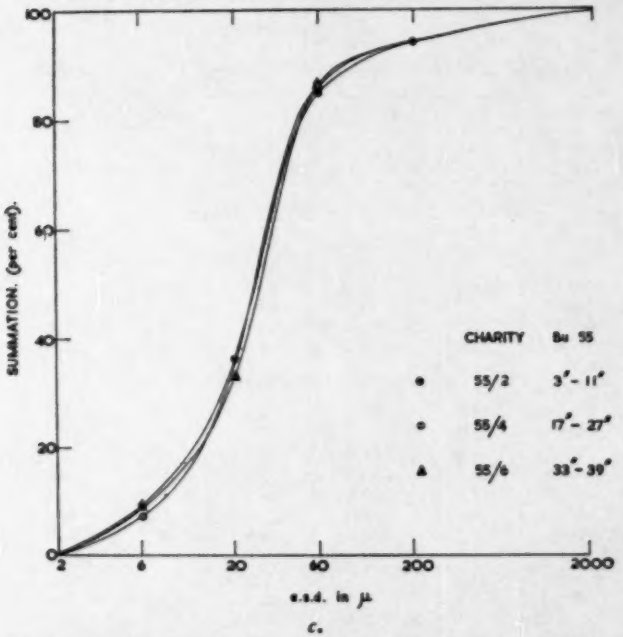
• Determined spectrographically in neutral $N.NH_4Ac.$ leachate.
† Cation-exchange capacity determined by estimation of ammonia displaced by a second leaching with 10 per cent. NaCl.


SUMMATION. (per cent).
100
80
60
40
20
0
2
6
20
60
200
2000
e s d in μ
BATCOMBE Bu 14.
14/2 11½° – 8°
14/4 16° – 29°
14/5 36° – 60°
14/6 78° – 90°

a.


SUMMATION. (per cent).
100
80
60
40
20
0
2
6
20
60
200
2000
e.s.d. in μ
WINCHESTER Bu 54.
54/2 24° – 7°
54/4 12° – 26°
54/6 37° – 43°

b.



c.

FIG. 2*a*, *b*, *c*. Summation curves of soil horizons on a clay-free basis.

is attached to the fine sand and silt fractions, since the coarse sands contain much mechanically weathered flint and up to 50 per cent. of concretions.

Fig. 2 reveals that samples from the Charity and from the upper 29 in. of the Batcombe have a similar particle-size distribution in the intermediate range, indicative of sorted material with a well defined maximum at around 60–20μ. These results conform with those obtained by Perrin (1956) for a topsoil overlying Clay-with-flints at Coombe Hill nearby, and suggest that the materials are at least partly derived from loess. In contrast the remaining curves reveal a more regular size distribution with indications of sorting only in the fine sand (200–60μ) grade. The lowest horizons of the Batcombe and Winchester profiles contain over 80 per cent. clay and resemble the Upper Chalk residues in this respect, but only the subsoil horizon of the Winchester adjacent to the Chalk has a mechanical composition consistent with a wholly residual origin. The overlying horizons of this profile and the subsoil of the Batcombe below 29 in. contain significant amounts of fine sand, localized to some extent in pockets, and most probably of Eocene derivation.

Petrographic studies

The fine sand (200–60μ) and coarse silt (60–20μ) separates were examined using standard petrographic techniques, after preliminary heavy liquid separation with bromoform (S.G. 2·90).

TABLE 2

Particle-size Distribution in Soils and Chalk Residues

Sample no.	Depth (in.)	Sand		Silt			Clay
		Coarse 2–0·2 mm.	Fine 200–60μ	Coarse 60–20μ	Medium 20–6μ	Fine 6–2μ	< 2μ
		Batcombe (Flinty) Silt Loam					
14/1	0–1½	3·0	6·7	42·9	25·2	8·0	14·2
14/2	1½–8	2·2	8·8	38·1	23·8	9·5	17·6
14/3	8–16	0·9	7·9	37·3	16·2	8·6	29·1
14/4	16–29	0·7	5·9	22·9	13·3	3·6	53·6
14/5	36–60	7·7	15·6	9·6	7·4	1·7	58·0
14/6	78–90	2·2	3·8	2·0	1·9	1·6	88·5
		Winchester Flinty Loam					
54/1	0–2½	12·0	14·7	19·3	27·6	10·4	16·0
54/2	2½–7	15·5	15·5	20·5	22·4	10·0	16·1
54/3	7–12	9·9	12·1	5·7	6·0	4·5	61·8
54/4	12–26	8·0	13·6	5·4	5·0	4·0	64·0
54/4a*	12–26	14·9	29·7	15·6	4·6	4·8	30·4
54/5	26–37	2·2	2·3	2·9	1·4	4·5	86·7
54/6	37–43	0·7	0·6	0·6	1·7	4·8	91·6
		Charity Flinty Silt Loam					
55/1	0–3	5·2	8·6	44·0	18·3	8·1	15·8
55/2	3–11	4·9	8·2	42·5	23·8	7·9	12·7
55/3	11–17	5·3	6·9	39·6	21·1	6·5	20·6
55/4	17–27	3·4	4·6	27·8	16·1	4·1	44·0
55/5	27–33	3·2	4·1	27·3	13·1	6·0	46·3
55/6†	33–39	3·9	4·9	33·0	14·9	5·5	37·8
		Chalk Residues					
C 1	..	0·6‡	0·4	0·5	0·7	0·3	97·5
C 2	..	..	0·3	0·7	0·5	5·8	92·7

* Sandy inclusion at 12–26 in.
† Carbonate-free material only.
‡ One grain only.

Light separates. Quartz, flint, and feldspar are the main detrital components, although their distribution varies widely: manganiferous concretions and nodules are locally abundant and muscovite and glauconite occur as accessories. Secondary silica (chalcedony), either rod-shaped or of mossy or botryoidal habit, is also present and is apparently of authigenic origin (Brown and Ollier, 1956*a*). In the surface horizons the silts contain small amounts of opal phytoliths (Smithson, 1958).

Flint is dominant in the subsoil of the Winchester below 26 in.: collophane identical with that from Chalk residues (Brown and Ollier, 1956*b*) is also present, supporting the view that the sand and silt fractions are largely Chalk-derived. Manganiferous concretions are also commonest in the Winchester and give the sands and silts a dark brownish or blackish appearance.

Quartz is dominant in the upper 26 in. of the Winchester and throughout the Charity and Batcombe profiles. Feldspar, including microcline, albite, and orthoclase, is common throughout the Charity and fairly common in the upper 29 in. of the Batcombe; small amounts also occur in the surface and subsurface horizons of the Winchester. In the remaining horizons of the Batcombe and Winchester feldspar is rare and its distribution in these profiles strongly suggests that the upper horizons have had additions of extraneous material.

Heavy separates. Opaques (mainly 'limonitic' with some ilmenite, magnetite, and haematite) are dominant in all the separates. In the Batcombe profile non-opaque heavy minerals common to all horizons are zircon, rutile, tourmaline, kyanite, and staurolite, but in the upper horizons the coarse silts, and to a lesser extent the fine sands, contain a more varied suite, including epidote-clinozoisite, garnet, chlorite, and green hornblende which are rare or absent in the substratum (Table 3, B and C). The same trend is shown in the Winchester, but only the upper 7 in. shows notable additions.

TABLE 3

*Distribution of Non-opaque Heavy Minerals (60–20μ)**

	A	*B*	*C*	*D*
%	*Reading Beds. Cowcroft (Grid Ref. SP/984018)*	*Batcombe (36–60″)*	*Batcombe (6–9″)*	*Charity (17–27″)*
> 50	zircon	zircon	..	..
25–50	..	..	zircon	zircon
10–25	rutile	rutile tourmaline	epidote rutile	epidote garnet
2–10	tourmaline staurolite kyanite	staurolite kyanite	tourmaline garnet chlorite hornblende staurolite kyanite	rutile chlorite tourmaline hornblende staurolite kyanite
< 2	epidote hornblende monazite brookite anatase	anatase brookite hornblende epidote garnet monazite	anatase brookite sphene monazite tremolite	anatase brookite sphene monazite tremolite

* The minerals listed are only those commonly occurring: other minerals of rare or sporadic occurrence include sillimanite, andalusite, chloritoid, glaucophane, spinel, and dumortierite. In each of the frequency groups shown the minerals are listed in order of abundance.

In the Charity the assemblage and relative abundance of minerals are similar throughout and are comparable to that found in the upper horizons of the other two profiles. The typical assemblage is shown in

Table 3, D, except for apatite which is present in the basal layers only: its absence in the upper horizons is undoubtedly due to its limited resistance to weathering.

Micromorphology

In each profile a thin acid mull or mull-like moder surface overlies a brown or yellowish brown sub-surface horizon of similar texture with a *braunerde*-like fabric (Kubiëna, 1953) characterized in thin section by uniformly distributed, unoriented clay: this is succeeded by brighter-coloured, finer-textured subsoil horizons with blocky structure, in which anisotropic clay with varying degrees of orientation is more or less irregularly distributed.

The Charity subsoil has a heterogeneous fabric resembling that described in B horizons of *parabraunerde* on loess by Kubiëna (1956*a*) and in grey-brown podzolic soils on calcareous till by Frei and Cline (1949). In contrast to the sub-surface horizon, part of the clay in the succeeding transitional horizon (11–17 in.) is anisotropic and has accumulated in roughly concentric layers in pores, while in the lower part of the subsoil (27–33 in.) moderately to strongly oriented clay forms veins up to ½ mm. thick, mainly devoid of primary mineral grains and partly filling wide channels.

The Winchester subsoil, by contrast, has a comparatively uniform *braunlehm* fabric. Primary mineral grains and ferruginous concretions are embedded in dense, yellowish brown, weakly oriented clay, containing irregular manganiferous segregations and intersected by shrinkage cracks. Locally stronger orientation is associated with pore-fillings and, particularly in the lower horizon, with flow structures.

The heterogeneous character of the Batcombe subsoil, clearly evident to the naked eye, is further revealed by thin-section studies. Particularly below 29 in., the fabric includes *braunlehm* and *rotlehm* elements similar to those described by Kubiëna (1956*b*), who considers rubefication as indicative of transformation under a warm climatic régime with marked wet and dry periods. Pores filled, or partially filled, with optically oriented yellowish brown clay are common at 16–29 in., while the uppermost part of the subsoil, at 9–16 in., includes relatively pale-coloured, clay-deficient zones and aggregate peripheries, as found in the B_1 horizons of strongly acid grey-brown podzolic soils by Frei and Cline (1949). In the deeper subsoil at 30–60 in. thick, bleached clay coatings with a high degree of optical continuity are frequently associated with conducting channels and cleavage faces.

Clay mineral analysis

The clay minerals were identified at group level from patterns of oriented aggregates taken in a 9·0 cm. diameter Bradley type camera with filtered CoKα radiation. Photographs were taken after glycerol treatment, and after heating overnight at 300° C. and at 540° C. For certain samples, photographs were taken of unoriented powders. The following criteria were adopted for the identification of minerals from the oriented aggregate patterns.

Montmorillonite Group minerals give a basal reflection at 17·8 Å. on glycerol treatment and a reflection at 10 Å. after heating at 300° C. and 540° C.

Vermiculite Group minerals give a basal reflection at about 14 Å. and a reflection at 10 Å. after similar heat treatments.

Mica Group minerals give a reflection at 10 Å. with all the above treatments.

Kaolin Group minerals give reflections at 7·1 Å. and at 3·56 Å. on glycerol treatment and also on heating at 300° C.: on heating at 540° C., the pattern is eliminated.

Chlorite Group minerals give a reflection at 14 Å. with all treatments, the intensity of this reflection being enhanced on heating at 540° C.*

From the 060 reflections obtained on powder patterns, all the 2 : 1 lattice clays appear to be dioctahedral. Semi-quantitative estimates of the crystalline clay minerals were obtained by comparing the visually-estimated intensity ratios of 10 Å. and 7 Å. reflections on photographs of glycerol-treated and 300° C.-heated specimens, assuming I_{10}:I_7 is 1 : 3 for equal amounts. This gives values for kaolin, mica, and expanding minerals, the latter being subdivided into montmorillonite and vermiculite on the basis of the 14 Å. and 17·8 Å. reflections obtained from glycerol-treated aggregates. Since there is no entirely satisfactory method for the quantitative analysis of clays even when few well-crystallized minerals are present, the figures only allow comparison of the proportionate amounts of layer-lattice silicates in successive horizons (Table 4).

In addition to the silicates, various accessories occur: quartz, anatase, and goethite are present in most of the clays, but quartz (at about 5 per cent.) is commonest in the surface and sub-surface horizons. Feldspar is also present in the surface horizon of the Batcombe and in both surface and subsoil of the Charity; calcite occurs in the substratum of this soil and apatite in the Chalk residues. Lepidocrocite is present throughout the Batcombe, being particularly prominent in the mottled subsoil horizons. After heat treatment at 540° C. all the clays containing identifiable crystalline iron oxides gave broad haematite reflections and in some these appeared to be stronger than would be expected from the amounts of goethite and/or lepidocrocite present in the original, suggesting the presence of more or less amorphous, hydrated iron oxides.

Discussion

Origin of soil-forming materials

The particle-size distribution and petrographic studies indicate that whereas the Charity is reasonably interpreted as an autochthonous profile resulting from the decalcification of chalky drift, the Batcombe and Winchester are composite profiles, the fine sands and silts of their upper horizons containing heavy residues of a mineralogical character different from those of the substrate and congruent with those of the entire Charity profile. This relatively fresh mineral assemblage, characterized by epidote-clinozoisite, garnet, chlorite, and green hornblende, and accom-

* Subsequent orders of the 14 Å. chlorite reflection can interfere with the identification of kaolin group minerals if chlorite is present in appreciable quantities, but only traces were identified in any of the clays examined.

TABLE 4

Clay-mineral Analyses

(Proportionate amounts of layer-lattice silicates expressed as parts of 10)

Profile and sample no.		*Depth (in.)*	Mo	Vm	M	Ka	Cl
Batcombe (flinty) silt loam	Bu 14/1	1–2	..	5	2	3	Tr.
	14/2	2–8	..	6	1	3	Tr.
	14/3	8–16	..	6	1	3	Tr.
	14/4	16–29	..	5	2	3	..
	14/6	36–60	..	3	3	4	..
	14/7	78–90	2	1	3	4	..
Winchester flinty loam	Bu 54/1	0–2½	Tr.	7	Tr.	3	..
	54/2	2½–7	Tr.	7	Tr.	3	..
	54/3	7–12	6	Tr.	1	3	..
	54/4	12–26	6	..	2	2	..
	54/4a*	..	3	3	1	3	..
	54/5	26–37	6	..	1	3	..
	54/6	37–43	6	..	2	2	..
Charity flinty silt loam	Bu 55/1	0–3	..	5	3	2	Tr.
	55/2	3–11	..	6	2	2	Tr.
	55/3	11–17	..	7	1	2	..
	55/4	17–27	..	3	5	2	..
	55/5	27–33	2	1	5	2	..
	55/6	33–39	4	..	4	2	..
Chalk residue	C 1	..	8	..	2	..	..
	C 2	..	8	..	2	..	..
Reading Beds	RB 1	..	6	1	2	1	..
	RB 2	..	4	Tr.	4	2	..
	RB 3	..	3	Tr.	5	2	..

Mo = montmorillonite; Vm = vermiculite; M = mica; Ka = kaolin; Cl = chlorite.
* Sandy material at 12–26 in.

panied by increased amounts of feldspar, is associated in each profile with sorted material rich in coarse silt, suggesting strongly that it originated in added loess. In the Charity profile, as in the 'loess-with flints' of northern France (Zeuner, 1945), admixture of loess with materials derived from Chalk or pre-existing plateau deposits may be attributed to solifluxion, heterogeneous deposits of this kind being particularly prevalent in regions where periglacial climates were characterized by relatively abundant snow-fall. In the Batcombe, the silty upper horizons of which contain small shattered flints similar to those in the Charity, incorporation of loess with the underlying Clay-with-flints probably results from solifluxion or frost action but may also have been effected by uprooting of trees and faunal activity. The results for the Winchester profile suggest that loess-derived material is confined to the upper 7 in. and is present in comparatively minor amounts: this layer, containing a high proportion of broken and corroded flints and appreciable amounts of flint and quartz sand, has the aspect of an erosion pavement (Shaw, 1929) from which fine material has been removed by deflation or lateral eluviation.

The flinty clay substrata of Batcombe and Winchester profiles, the intensively weathered character of which is attested by the comparative rarity of feldspar in sand- and silt-size fractions, appear to contain Chalk- and Eocene-derived materials in varying proportions. The Batcombe subsoil below 29 in., like the sandy inclusions in the Winchester, contains only scattered flints and is characterized by a mineral assemblage comparable with that of Reading Beds sands at Lane End (Wooldridge and Ewing, 1935) and at Cowcroft, Bucks. (Table 3, A), and as both plateau profiles are located well above the early Pleistocene shore-line (Wooldridge, 1957), this is the most likely source of fine sand. The extent to which the irregularly rubefied fabric of the Batcombe subsoil, characteristic also of plateau drift in Kent (Dalrymple, 1958), is inherited from sediments of Reading Beds age, cannot be ascertained from this investigation, but the sub-plastic and pervious nature of the drift and its relatively high kaolin and low montmorillonite content, as compared with the Reading Beds clays examined, suggest that it has been subjected to further weathering in later Tertiary or interglacial periods. The occurrence of 'lateritic' concretions in the Winchester profile and the presence of significant amounts of secondary chalcedonic silica, probably derived ultimately from corroded flints, are also indicative of advanced weathering.

By contrast with the Batcombe subsoil, that of the Winchester is rich in montmorillonite, with kaolin and mica subsidiary, and has a comparatively uniform *braunlehm* fabric resembling that of *Terra Fusca* (Kubiëna, 1953): somewhat sandy in the upper part, the clay becomes increasingly homogeneous as the Chalk is approached and contains only scattered mineral grains, notably of flint and collophane which are certainly Chalk-derived. The presence of a similar horizon under the Batcombe profile in contact with the Chalk surface would be expected from observations elsewhere (cf. Barrow, 1919) and is indicated by the occurrence below 60 in. of montmorillonite in association with decreasing sand content and numerous large, little-broken flints. These results suggest that Clay-with-flints *sensu stricto*, as represented by the clay-rich Winchester subsoil, is residual from Chalk, but its derivation by oxidative weathering of montmorillonitic and micaceous clay residues (see Table 4) necessitates the formation of kaolin, as well as appreciable relative accumulation of ferric hydroxide (Brajnikov, 1937), thus involving significant losses of silica, and hardly consistent with survival of collophane. Even without weathering loss, accumulation of the thicknesses encountered would generally require the dissolution of considerably more chalk than is reasonably allowable on geomorphic grounds (cf. Jukes-Brown, 1906), so Barrow's contention that the clay is largely derived from overlying deposits clearly merits consideration. The horizon adjacent to the Chalk frequently exhibits slickensided fissures indicative of irregular subsidence, together with flow structures and cavity fillings most readily explicable as resulting from the more or less selective infiltration of semi-fluid clay into spaces left by solution. It has also been suggested (Brajnikov, 1937) that, besides favouring the segregation of manganese into concretions, the cation concentration gradients associated with the Chalk

junction may lead to the reconstitution of clay minerals, particularly montmorillonite, from weathering products dissolved or suspended in the drainage water. Formation of Clay-with-flints *sensu stricto* involving such processes could have proceeded during Tertiary or interglacial periods wherever, under humid climatic conditions, the Chalk underwent long-continued and undisturbed dissolution beneath a weathered, pervious cover capable of supplying appreciable amounts of clay. Much of the Tertiary product appears to have been rearranged and mixed with other sediments, thus constituting the Clay-with-flints *sensu lato* of Sherlock (1947), but that which lines the Chalk junction beneath highly weathered plateau drifts and slope deposits containing far-travelled stones (cf. Barrow, 1919) must clearly have originated in Pleistocene times. This phase of Clay-with-flints formation, which in the region east of Marlow is well represented on surfaces bevelling dissected relics of the Harefield terrace (Wooldridge, 1957), seems to imply an extended period of undisturbed weathering under warm-temperate climatic conditions, which predated the main Chalky Boulder Clay (Catuvellaunian) glaciation.

Profile development

Particle-size data for the Charity profile indicate a distinct clay maximum in the subsoil, attributable to translocation, weathering, or clay-mineral synthesis (cf. McCaleb and Cline, 1950). The non-uniform distribution, location, and optical continuity of oriented clay strongly suggest that textural differentiation is due mainly to deposition of eluviated clay which may either have been inherited from the mixed parent material or produced, in limited amounts, by dissolution of chalk or by weathering of sand- and silt-size silicates of loessial origin. In addition, clay-mineral analyses give clear indications of weathering trends affecting the layer-lattice silicates. Thus, while montmorillonite and mica predominate in the chalky substratum, the proportion of the former decreases rapidly upwards and dioctahedral vermiculite increases to become the dominant mineral in upper subsoil and sub-surface horizons: kaolin occurs in moderate amounts throughout and is probably inherited. These results suggest alteration of montmorillonite and mica and accumulation of vermiculite which appears to constitute a relatively stable phase of expanded 2:1 lattice clay in well drained, acid soils low in exchangeable calcium. The mineral referred to here as vermiculite may well be closely related to the minerals described by Brown (1954), Rich and Obenshain (1955), Tamura (1958), and Sawhney (1958), in which more or less complex, basic aluminium ions, derived by weathering of either primary silicates or clay-minerals under acid conditions, are apparently sorbed between the layers.

Particle-size and petrographic data for the Batcombe profile, indicating the presence of loessial material to at least 29 in., suggest that the marked textural change between 8 and 16 in. is mainly pedogenic, superimposed on that resulting from the incorporation of loess. This is confirmed by thin section studies giving evidence of recent clay migration through fissures and old root holes: seasonal stagnation in these conducting channels of water containing reducing substances is probably responsible

for the associated bleaching in the deeper subsoil, which generally extends into the matrix beyond the zone of preferred orientation. It is also noteworthy that the upper horizons of this profile, resembling the Charity in particle-size distribution, show similar trends in clay-mineral constitution, the maximum concentration of vermiculite being located in sub-surface and upper subsoil horizons where exchangeable calcium and degree of saturation are at a minimum. Areas virtually depleted of clay-size material, interpreted as zones of clay destruction by Frei and Cline (1949), are associated with aggregate peripheries in the upper part of the subsoil, and are much more conspicuous in other profiles of this series, constituting a distinct, though often discontinuous, horizon several inches thick. Such horizons, which generally contain small ferri-manganiferous concretions, appear to be associated with intermittent waterlogging due to restricted drainage, and this may lead, as in planosols, to accelerated loss of silicate clay by weathering under conditions which favour sustained saturation with acid solutions while allowing removal of decomposition products (cf. Jackson *et al.*, 1948).

The evolution of the Winchester profile, occupying an upper slope position subject to erosion and soil creep, has evidently followed a somewhat different course, since the sharp boundary at 7 in., marked by a fourfold increase in clay content and a considerable change in the distribution of sand- and silt-size separates, can hardly be attributed to pedogenic agencies alone. As against this, the surface and sub-surface horizons resemble those of the other two profiles in morphology and clay mineralogy, suggesting that essentially similar processes of clay depletion, coupled with acidic weathering and vermiculite accumulation, have operated in each profile.

Thus, although all three profiles have weak-structured sub-surface horizons, conventionally designated A_2 or A_3 (Mückenhausen, 1957), typical of *sols lessivés* as defined by Duchaufour (1956), only in the Charity, which conforms most closely to the grey-brown podzolic (*parabraunerde*) concept, is there a clear illuvial B horizon. The Batcombe and Winchester, resembling red-yellow podzolic soils, are apparently 'two-stage' profiles (Polynov, 1927) in which textural differentiation has been superimposed on a composite (non-uniform) parent material resulting from the addition of loess to the truncated or redeposited remains of previously weathered horizons with *rotlehm* and/or *braunlehm* fabrics. However, as the land surfaces concerned have presumably been subjected to at least one alternation of periglacial and temperate conditions after the accumulation of loess, the extent to which either profile reflects the influence of the contemporary environment is not readily assessed, but the indications are that the upper horizons bear the impress of similar pedogenic processes, modified in the Winchester by the effects of erosion and soil creep.

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REFERENCES

ARKELL, W. J. 1947. The Geology of Oxford. Clarendon Press, Oxford.

AVERY, B. W. 1958. A sequence of beechwood soils on the Chiltern Hills, England. J. Soil Sci. **9**, 210–24.

BARROW, G. 1919. Some future work for the Geologists' Association. Proc. Geol. Ass. Lond. **30**, 36–48.

BRAJNIKOV, B. 1937. Recherches sur la formation appelée 'Argile à silex' dans le Bassin de Paris. Rev. Geogr. Phys. **10**, 7–90, 109–29.

BROWN, G. 1954. Soil morphology and mineralogy. A qualitative study of some gleyed soils from North-west England. J. Soil Sci. **5**, 145–55.

—— and OLLIER, C. D. 1956*a*. Secondary silica in soils (unpublished manuscript).

—— —— 1956*b*. Collophane from the Chalk. Min. Mag. **31**, 339–43.

CHARLESWORTH, J. K. 1957. The Quaternary Era. Edw. Arnold, London.

CODRINGTON, T. 1865. The Geology of the Berks. and Hants. Extension and Marlborough Railways. Wilts. Archaeol. Nat. Hist. Mag. **9**, 167–93.

DALRYMPLE, J. B. 1958. The application of soil micromorphology to fossil soils and other deposits from archaeological sites. J. Soil Sci. **9**, 199–210.

DOUBLE, I. S. 1927. The microscopic characters of certain horizons of the British Chalk. J. R. Micr. Soc. **47**, 226–31.

DUCHAUFOUR, P. 1956. Pédologie: Applications forestières et agricoles. Ec. Eaux. For., Nancy.

FREI, E., and CLINE, M. G. 1949. Profile studies of normal soils of New York. II. Micromorphological studies of the grey-brown podzolic–brown podzolic sequence. Soil Sci. **68**, 333–45.

JACKSON, M. L., TYLER, S. A., WILLIS, A. L., BOURBEAU, G. A., and PENNINGTON, R. P. 1948. Weathering sequence of clay-size minerals in soils and sediments. J. Phys. Chem. **52**, 1237–60.

JUKES-BROWN, A. J. 1906. The 'Clay-with-flints', its origin and distribution. Quart. J. Geol. Soc. London, **52**, 132–64.

KUBIËNA, W. L. 1953. The Soils of Europe. Murby, London.

—— 1956*a*. Zur Micromorphologie, Systematik und Entwicklung der rezenten und fossilen Lössböden. Eiszeitalter und Gegenwart, **7**, 102–12.

—— 1956*b*. Rubefizierung und Laterisierung (zu ihrer Unterscheidung durch mikromorphologische Merkmale). Trans. Sixth Int. Congr. Soil Sci. **E**, 247–9.

MCCALEB, S. B., and CLINE, M. G. 1950. Profile studies of normal soils of New York. III. Physical and chemical properties of brown forest and grey-brown podzolic soils. Soil Sci. **70**, 315–28.

MÜCKENHAUSEN, E. 1957. Die wichstigsten Böden der Bundesrepublik Deutschland. Wissenschaftliche Schriftenreihe des A.I.D. Heft 14.

OAKLEY, K. P. 1936. Field meeting at Cheddington, Ivinghoe and Gubblecote. Proc. Geol. Ass. Lond. **47**, 38–41.

PERRIN, R. M. S. 1956. The nature of 'chalk heath' soils. Nature, Lond. **178**, 31–32.

POLYNOV, B. B. 1927. Contributions of Russian Scientists to Paleopedology. Russian Pedological Investigations, **8**, Acad. of Sci., U.S.S.R.

RICH, C. I., and OBENSHAIN, S. S. 1955. Chemical and clay-mineral properties of a red–yellow podzolic soil derived from muscovite schist. Proc. Soil Sci. Soc. Amer. **19**, 334–9.

ROBINSON, G. W. 1949. Soils, their Origin, Constitution and Classification. Murby, London.

SAWHNEY, B. L. 1958. Aluminium interlayers in soil clay minerals, montmorillonite and vermiculite. Nature, Lond. **182**, 1595–6.

SHAW, C. P. 1929. Erosion pavement. Geogr. Rev. **19**, 638–41.
SHERLOCK, R. L. 1947. British Regional Geology. London and the Thames Valley. Mem. Geol. Surv. U.K.
SMITHSON, F. 1958. Grass opal in British soils. J. Soil Sci. **9**, 148–54.
SPARKS, B. W., and LEWIS, W. V. 1957. Escarpment dry valleys near Pegsdon, Hertfordshire. Proc. Geol. Ass. Lond. **68**, 26–38.
TAMURA, T. 1958. Identification of clay minerals from acid soils. J. Soil Sci. **9**, 141–7.
TAVERNIER, R., and SMITH, G. D. 1957. The concept of braunerde (brown forest soils) in Europe and the United States. Advanc. Agron. **9**, 217–89.
WHITAKER, W. 1889. Geology of London and of part of the Thames Valley, Vol. I. Mem. Geol. Surv. U.K.
WOOLDRIDGE, S. W., and EWING, C. J. C. 1935. The Eocene and Pliocene deposits of Lane End, Buckinghamshire. Quart. J. Geol. Soc. Lond. **91**, 293–317.
—— and LINTON, D. L. 1955. Structure, Surface and Drainage in South-east England. George Philip, London.
—— 1957. Some aspects of the physiography of the Thames Valley in relation to the Ice-age and early man. Proc. Prehist. Soc. **23**, 1–19.
ZEUNER, F. E. 1945. The Pleistocene Period. Its climate, chronology and faunal successions. Ray Society, London.

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SOIL CLASSIFICATION—A DESTRUCTIVE CRITICISM

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Summary

Attention is drawn to the theoretical and practical errors associated with the use of the profile as the working tool of soil classification. It is claimed that the planar characteristics of the profile are fundamentally inappropriate for depicting the four-dimensional qualities of soil. The concept of the modal profile is discussed, in particular its role in encouraging a 'calculus' approach to a soil classification constructed from an infinite number of finite units. It is suggested that a workable system of soil classification will be possible only by adopting some new approach completely free of the basic defects of the 'soil-profile' approach.

It is pleasing to find that the *Journal of Soil Science* is permitting room for the airing of controversy in that most controversial of worlds, the world of soil classification (Leeper, 1956; Kubiëna, 1958). It would seem therefore somewhat audacious of Leeper in his paper to add to controversy by also classifying pedologists. In his classification he has completely omitted those pedologists who neither accept that great men have necessarily done the main job, nor are prevented by dignity from accepting any approach to the subject—genetic or otherwise. They simply request that the approach shall satisfy fully their critical faculties and shall not in any way offend the tenets of their basic training. A critical and logical analysis of the general situation as it appears to one such pedologist is therefore probably appropriate, using the two recent papers by Leeper and Kubiëna as a basis for discussion.

Moral support for this criticism comes partly from Leeper himself, who admits that great men have not simplified soil classification but have brought a degree of confusion which is the despair of the critical reader. In much the same way Liebig's unsympathetic approach to the work of Boussingault confused the issue, and resulted in fifty years of delay before the fixation of nitrogen was grasped. Yet Sir Lawrence Bragg (quoted in *Chem. Eng. News*, 21 January 1958, p. 26) states: 'The work of the past is of course the foundation on which further advance has been made, but it is dead; it has been replaced by a more complete understanding.' To what extent therefore are we to depend on the past in clarifying our ideas on soil classification; and what are we to cast aside in the light of more complete understanding?

One of our most important inheritances from the past is the soil profile. In fact an ever-increasing degree of appreciation of the profile has moved hand-in-hand with the general progress that has been made in soil science The question arises, is the usefulness of the profile in soil science overplayed, particularly in clarifying our views on classification?

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Is there a confusion, albeit a subconscious one, between the need for the profile in understanding pedogenesis and its use in soil classification? The importance of understanding pedogenesis seems obvious, but, as has been repeatedly said, it is not logically necessary to invoke pedogenesis as a basis for classification. The question indeed arises why the protagonists of the non-genetic approach to classification even choose the profile as a basic unit. It is not necessarily logical to do so since even profile morphology, either on the restricted basis of Leeper or on the ideally comprehensive basis of Kubiëna, is inevitably tinged with a visual manifestation of pedogenesis. Leeper acknowledges that classification need have nothing to do with soil mapping. In a sense this is appreciated, but if soil profiles constitute the basis of mapping and if classification is based on soil profiles either morphologically or genetically, somewhere along the line of reasoning the two issues are inextricably bound, possibly to an extent that may thwart all hopes of soil classification.

Leeper attributes much of the confusion to a confusion of soil with land or landscape, and admits that his article deals with the classification of soil profiles and not types of land. Then why, the question may be asked, does he entitle his paper 'Soil Classification' and not 'Soil-Profile Classification'? The answer is because he calls them one and the same thing.

In science, definitions are the precise building bricks in the solid foundations of logical argument. An appropriate definition of a soil profile would appear to be: 'A soil lamina with empirical width and depth aligned radially towards the centre of the earth.' The Multilingual Vocabulary of Soil Science (F.A.O., 1954) refers to the soil profile as a 'vertical section'. The profile is essentially then a two-dimensional entity. Why therefore it should be expected to provide a satisfactory basis for classification of soils—and soil is essentially a three-dimensional continuum—defies understanding. Leeper readily contends he is dealing with the classification of soil profiles. That statement in itself is accepted, but his right to extrapolate his working principles to the problem of soil classification must be contested. He undertakes this step, claiming that 'the same principles apply to the larger problem though a different coding system would be called for'—a relatively simple verbal transformation from two to three dimensions that defies mathematical perception.

Let us consider a point in space (and excluding the time dimension) of coordinates (x, y, z). More precisely let this point be anywhere within the soil mass. It may then be represented by the equation:

$$ax^3+by^3+cz^3+\dots .$$

A transformation of this equation to two dimensions means that one coordinate becomes zero and the equation reduces to:

$$Ax^2+By^2+\dots .$$

This essentially defines the coordinates of a point (x, y) lying in one plane. In the present context such a point will lie in the vertical section of the soil profile. The properties associated with the point (x, y) will now only be those operating vertically through the planar disposition of

(x, y). That is to say, soil behaviour at that point is strictly a function of those soil-forming factors which operate more or less vertically within the plane containing (x, y), i.e. the soil profile. It follows logically and inevitably that if profiles are to form the basis of soil classification, the question of soil-forming factors other than those functioning strictly vertically must be dispensed with. As a necessary consequence soil classification can only be constructed from soil profiles essentially developed *in situ*.

Such a conclusion is untenable in several ways. It implies, for example, that the influence of relief on soil development should no longer be recognized. The time factor in soil development should also be discarded since time and relief interact strongly in their respective roles both in pedogenesis and in profile morphology. It follows that soil depth should be uniform together with the original surface configuration of the parent rock which initially formed the soil parent material. By further reasoning we must also accept that *in-situ* development in the absence of any effects from relief and time will preclude the existence of any intergrading between one characteristic soil profile and the next. By the same line of reasoning we refute the existence of both the colluvial and the alluvial site, a fact of such serious implication in the practical application of pedology that it alone justifies a return to our original premises and viewing them again in the light of greater understanding.

The essential three-dimensional quality in the soil mass reveals still another weakness in adopting the profile as the basis of soil classification. This weakness is perhaps best emphasized by comparing the present method of soil classification with that adopted in botany. The botanical approach is strictly practical, as Leeper admits, but whereas it is possible in botany it is essentially incorrect in pedology. Flowers and plants are in themselves discrete entities. Separate flowers remain separate biological systems in spite of cross pollination and hybridization, and depend in their ultimate performance on their own separate reactions to a particular ecological environment. In so far as they may contain within themselves striking similarities they may be classified together. If they differ in some small respect they may be classified separately. Analagous circumstances, however, do not occur in soils. No soil possesses a discrete existence but merges imperceptibly into the soil in juxtaposition with it.

To overcome this difficulty pedologists have postulated a modal profile. This endows a three-dimensional quality on the essentially two-dimensional character of the profile, accomodating thereby the intergrade between one modal profile and the next. Variants about the modal profile occupy positions relative to the modal profile in much the same way as the extremes of variability fall on the outer quartiles of the Gaussian distribution curve of errors. This concept has proved extremely useful in practical mapping and has certainly simplified the task of the soil surveyor. It has, however, been one direct cause of introducing an indescribable degree of complexity into soil classification. It can easily be appreciated that the complete range of any modal quality at each level of the classification will decrease as one approaches the lower

orders of the classification. It must eventually then become extremely difficult, if not impossible, to recognize either the extremes of the modal quality or even the modal expression itself. No soil property has a discrete or circumscribed existence. Instead, it moves immediately and imperceptibly either in the direction of greater intensity or towards complete absence. In the latter case it is currently and continuously merging into some new property.

This state of affairs enforces upon our thinking a kind of 'calculus' outlook in which we aim to build the structure of our classification from an infinite number of finite units. As in the calculus, too, the interval between each finite unit must be regarded as sufficiently small that in the ultimate summation the final structure will be endowed with a quality of continuity. In this manner the discrete quality of the soil profile is overcome and the three-dimensional quality of the soil mass as a whole is recognized.

As a theoretical exercise this approach is extremely attractive, but as a practical means of establishing a soil classification it is extremely cumbersome and guilty of muddled thinking. It must inevitably mean that a successful soil classification, at least one in which we can place much confidence, will not become possible until the earth's surface becomes littered with an astronomical number of profile pits. Theoretically, the 'pedological interval' between these profile pits will require to be negligible if the final summation is to end in a complete soil classification. Again copying from the calculus, the theoretical quality of the infinitely small interval may be discarded and a near approximation permitted for the sake of arriving at a sensible answer. We are still left, however, with a prodiguous task. In fact it is reasonable to question whether we shall ever arrive at a workable classification in adopting this approach.

Kubiëna, in his criticism of Leeper, does not better the situation in this respect. A bag containing 200 marbles might be classified as follows according to the 'artificial' system of Leeper or the so-called 'natural' system of Kubiëna:

	Leeper	*Kubiëna*
Individuals	Marbles	Marbles
Number . .	200	200
Colour . .	..	3 Red White Blue
Size . . .	..	..
Bulk density .	..	..

According to Leeper's method the marbles have been arbitrarily classified according to one property. By Kubiëna's method classification has been extended to include additional properties; the ultimate number of properties adopted will be limited only by the 'actual stage of knowledge'. Kubiëna's viewpoint is clearly only an extension of Leeper's and the difference between the two is one of degree and not of approach. To postulate an 'artificial' as distinct from a 'natural' system is quite unsound and unnecessary, only intensifies the complexity that already exists, and adds still further to the 'despair of the critical reader'.

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The situation has clearly become too complex to remain scientifically sensible. Since classification must necessarily involve the systematic organization of individual units, it is questionable whether any form of systematics is applicable to soils, as they are not circumscribed units. It is fundamentally unsound to accept the soil profile as an expression of soil cover, since soil is essentially a part of landscape and a soil classification must contain within itself an inherent reflection of three dimensions. Some workable system is however required, and this will only be possible on the basis of a completely new approach that will successfully avoid the basic defects of the old approach. In the hope of fostering a new approach, it has been the purpose of this paper to expose the theoretical and practical errors associated with the adoption of the soil profile as the working tool of soil classification. The closest approach to truth so far would seem to be an alteration of Leeper's own words, viz.: 'The fog that envelops our subject comes from the confusion of soil profile with soil.'

REFERENCES

FOOD AND AGRICULTURE ORGANIZATION. 1954. Multilingual Vocabulary of Soil Science, p. 183.

KUBIËNA, W. L. 1958. The classification of soils. J. Soil Sci., **9**, 9.

LEEPER, G. W. 1956. The classification of soils. Ibid., **7**, 59.

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SOME MEASUREMENTS OF AIR SPACE IN SCOTTISH SOILS

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Summary

Total air-space values are related to the hydrologic sequence of soils as described by Glentworth and Dion. The greatest differences within the profile are found in freely drained soils, where from a value of approximately 50 per cent. air space in the B_2 horizon there is a drop to 25–35 per cent. (depending on the type of parent material) in the indurated B_3 horizon. Imperfectly drained soils have a slightly lower air space in the B_2 horizon and values decrease below. Poorly drained soils commonly have values between 35 and 40 per cent. and very poorly drained soils values between 30 and 35 per cent. The tendency for values to decrease in the lower horizons of a gley profile becomes less as the natural drainage conditions deteriorate.

Introduction

THE object of this work was to investigate the relation between soil air space and the hydrologic sequence of soils. Samples were collected as opportunity permitted during soil-survey seasons 1949–57 and laboratory determinations were made during the winter months.

The choice of a suitable method was conditioned by the need to obtain a significant number of comparable results within a reasonable period of time. That of Russell and Balcerek (1944) involving immersion of soil clods in paraffin was eventually adopted. All determinations were made on clods of earth up to about 100 g. in weight, after air-drying and then oven-drying at 105° C. In most cases each quoted horizon value is the average result derived from six clods.

The hydrologic sequence of soils developed on a particular type of parent material is referred to as a Soil Association (Glentworth and Dion, 1949). Each association, where fully developed, may be divided up into drainage series whose number may be adjusted in accordance with the scale of mapping. On a one-inch-to-one-mile scale map it is usual to separate freely drained, imperfectly drained, poorly drained, and very poorly drained soil series. In Scotland freely drained soils are podzols or less commonly brown forest soils; imperfectly drained soils are podzols or brown forest soils with gleyed B and C horizons, poorly drained soils are dominantly non-calareous gleys, and very poorly drained soils, with occasional exceptions, are peaty gleys.

Total air space in the hydrologic sequence. To relate these series within a hydrologic sequence, representative profiles of each series developed were sampled, the samples being taken from the horizon immediately below the plough layer or surface horizon in an arable soil, or from an approximately equivalent horizon in an uncultivated or semi-natural profile. The plough layer of arable soils was considered an unsuitable horizon for comparison because its structure and consequently its total air space (approximately equivalent to total pore space) is conditioned more by seasonal cultivation and general farm-management practice

than by hydrologic conditions. Such considerations do not apply so closely to the horizon immediately below the plough layer, though there are occasions on which they cannot be ignored entirely (see below).

For the immediate sub-surface horizon the usual trend was a steady reduction in air space from about 50 per cent. or more at the freely drained end to about 30 per cent. at the very poorly drained end of the sequence; some examples of complete or partial sequences are quoted below.

TABLE 1

Air-space Values from the B_2 and Bg Horizons of Soils of Different Drainage Series on Various Parent Materials

	Freely drained (%)	*Imperfectly drained* (%)	*Poorly drained* (%)	*Very poorly drained* (%)
Cultivated soils				
Wood of Aldbar (Angus). Parent material: modified till derived from Lower O.R.S. strata .	49·4±0·6	37·2±1·1	30·8±0·4	..
Balcalk Farm (Angus). Parent material: till derived from flaggy and shaly beds of Lower O.R.S. age. . .	52·7±0·5	48·0±0·5	42·5±0·4	..
Sourhope Farm (Roxburghshire). Parent material: till derived from andesitic lava .	45·7±0·7	41·9±0·8	37·5±0·3	..
Parkhead Farm (Aberdeenshire). Parent material: till derived from granite and granitic gneiss. . . .	53·3±1·1	43·5±0·4	30·9±0·6	27·8±0·5
Auchmacoy (Aberdeenshire). Parent material: varved lacustrine clays.	..	..	37·9±0·3	30·2±0·3
Greenhall Farm (Aberdeenshire). Parent material: till derived from basic igneous rocks.	50·8±0·5	..	39·4±0·7	..
Whitemires Farm (Aberdeenshire). Parent material: till derived from basic igneous rocks.	..	..	37·9±0·4	33·8±0·4
Semi-natural soils				
Milton Farm, Tarfside, Glen Esk (Angus). Parent material: till derived from acid schists.	63·7±1·1	51·9±1·2	43·9±1·7	29·4±0·6
Wigg Burn, Wauchope Forest (Roxburghshire). Parent material: till derived from Silurian shales and greywackes .	54·8±0·7	..	45·5±0·8	38·1±0·7

This development is dependent on a reasonable uniformity of environment throughout any particular sequence. Irregularities are introduced when local variations in soil parent material or unusual agricultural activities occur (in particular the localized effects of compaction or disturbance caused by heavy machinery or land drainage operations).

Where low air-space values are found below the plough layer of a freely drained cultivated podzolic soil, they generally reflect the local elimination of the friable B_2 horizon of the original podzol profile and its incorporation in the surface soil by regular ploughing and cultivation coupled with slow downhill creep of surface soil. The low air-space value is therefore that of the upper part of the compact indurated B_3 horizon which is normally encountered below the friable B_2 horizon (particularly in north-east Scotland), e.g. in the sequence at Millhill Farm, Aberdeenshire. The sequence from Foodie Farm, Fifeshire (Table 2), shows a similar phenomenon.

TABLE 2

	Freely drained (%)	*Imperfectly drained* (%)	*Poorly drained* (%)	*Very poorly drained* (%)
Millhill Farm (Aberdeenshire). Parent material: till derived from granite and basic igneous rocks	25·5±0·5	39·6±1·4	32·1±0·5	33·7±0·8
Foodie Farm (Fifeshire). Parent material: till derived from andesitic lavas . . .	33·9±0·8	39·7±0·5	35·4±0·9	..

On the uncultivated wooded hilltop above the arable fields on which this sequence was developed an excessively freely drained semi-residual soil had a total air-space value of 59·4±0·7 per cent. at an equivalent depth in the profile.

Variations in air space encountered within the imperfectly drained series, particularly in the more strongly podzolized regions such as north-eastern Scotland, are traceable to mixed genetic origin.

The more 'freely drained' soils have podzolic profiles with partially gleyed B horizons, while the more 'poorly drained' ones are weak gleys. The former usually possess an indurated B_3 horizon, whilst the latter do not. This series is therefore particularly sensitive to the effect of localized variations in topography and parent material, and on a moderate hillslope total air-space variations within the mapped limits of the series may be somewhat irregular. The hydrologic sequence at Alten Farm, near Inverurie in Aberdeenshire, illustrates this point.

In this sequence it will be noted that the imperfectly drained soil (top field) has had its B_2 horizon eliminated by cultivation.

Samples taken from different profile pits in the same sequence on another occasion gave the following results:

Freely drained: 52·8±1·1 per cent. Poorly drained: 42·1±0·3 per cent.

TABLE 3

Alten Farm, near Inverurie Aberdeenshire. Parent Material: Till derived from Acid Schists and Basic Igneous Rocks

(*Uncultivated*) *Excessively freely drained* (%)	*Freely drained* (%)	*Imperfectly drained* (%)		*Poorly drained* (%)	*Very poorly drained* (%)
		Top field	*Bottom field*		
56·1±1·0	53·8±0·4	34·4±1·6 (top of B_3 horizon of podzolic profile)	51·5±1·2 (weak gley soil)	41·0±0·5	31·6±0·6

The poorly drained series, where mapped as a low humic gley, presents relatively few total-air-space anomalies. The measured value may show a good deal of variation between different sequences, but the relative values within a sequence are quite regular.

A subgroup of poorly drained soils which are peaty gleys has, however, been distinguished in the higher-rainfall areas of Scotland (i.e. over 40 in. annual rainfall), such as the west of Scotland and parts of the Border country. It has been noted that, where two such poorly drained profiles have been sampled in the same general locality, there is a tendency for the peaty gley to have a higher total-air-space value in the upper horizons of the profile; as, for example, in the sequence at Paddock Slack in the Border country.

TABLE 4

Paddock Slack (Selkirkshire). Parent Material: Till derived from Silurian Shales and Greywackes

Freely drained (%)	*Imperfectly drained* (%)	*Poorly drained* (%)	
		Low humic gley	*Peaty gley*
40 to 58*	49·3±0·7	43·7±0·8	47·5±1·5

* Samples very friable and fragile; low values due to crumbling.

Further data on poorly drained soils developed on this parent material will be found in Table 9.

It would be unwise to draw any definite conclusion from the evidence available, but it is suggested that the humus top of the peaty gley may provide a resilient blanket protecting the upper mineral horizons of the profile from the compacting effects, which can be severe in a high-rainfall area, of livestock and machinery. This suggestion is reinforced to some extent by data relating to an agriculturally drained, very poorly drained soil with an 8-in. mineral surface soil and a peaty-topped, very poorly drained soil with an 11-in. peaty surface soil in a sequence at Tillycorthie Farm, Aberdeenshire (*c.* 32 in. rainfall).

TABLE 5*

Tillycorthie Farm, Aberdeenshire. Parent Material: Till derived from Schists and Basic Igneous Rocks

Freely drained (%)	*Poorly drained* (%)	*Improved, very poorly drained* (%)	*Very poorly drained* (%)
47·8±0·6	33·7±0·1	30·5±0·5	32·1±0·9

The two very poorly drained profiles are at the edge of what was once a small peat moss, subsequently cut over and cultivated. Earlier cultivation and more mechanical compaction may well have been the fate of the 'improved' soil here, though it must also be borne in mind that the upper horizons of the peaty topped soil may be somewhat alluvial. For example, in the Millhill sequence (Table 2) the field textures of the freely and imperfectly drained soils are recorded as fine sandy loam, that of the poorly drained soil as loam, and that of the very poorly drained soil as sandy loam to loamy sand; and this is reflected in the air-space data. Unusually high air-space values for very poorly drained soils may also result from a high organic-matter content in the first mineral horizon of the profile, oven-drying of the sample clods at 105° C. being liable to produce shrinkage voids. This is believed to have happened in the Wigg Burn, Wauchope Forest sequence (Table 1). The figure of 38·1±0·7 per cent. total air space for the very poorly drained series is a high one; this horizon was observed to have rather a high organic-matter content when it was sampled.

The Individual Profiles of the Hydrologic Sequence

Freely drained soils

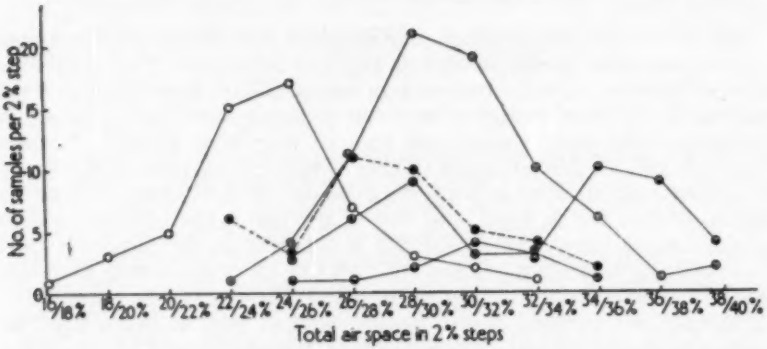
The freely drained podzolic profile, particularly as developed in north-east Scotland, consists of a raw-humus surface layer underlain by a grey leached A_2 horizon. Underneath the A_2 lies a friable B_2 horizon, whose structure becomes more cloddy towards the base, and merges fairly sharply into a compact indurated B_3 horizon below. Chemically the picture is one of the breakdown of the clay fraction in the leached A horizons into bases and sesquioxides of iron and aluminium. The bases leach out of the profile, the mobilized iron oxide and most of the alumina precipitate and accumulate in the B_2 horizon, whilst in the B_3 horizon the remainder of the alumina collects.

Air-space data reflect the sharp discontinuity between the friable B_2 and the indurated B_3 horizon (Table 7). Below the B_3 horizon, however, there is usually no obvious discontinuity between the total air space of the B_3 horizon and the underlying B/C or C-horizon material; there may be either a rise or a fall, or no marked change. Any difference in total air space between the B_3 and C horizon of the profile due to the actual 'induration' of the B_3 horizon must therefore be of relatively small magnitude. This indication is somewhat strengthened when the effect

* See also Table 10.

of parent material on total air space in the indurated layer is considered for acid, intermediate, and basic parent materials.

In Fig. 1 all the individual determinations available of total air space on indurated layers developed on four separate kinds of parent material have been presented in histogram form. From these histograms approximations to the modal values of total air space for indurated layers developed on these four parent materials may be obtained. The result for



○ Countesswells Association. Till derived from granite and granite gneiss.
⊙ Balrownie Association. Modified till derived from L.O.R.S. strata.
⊕ Tarves Association. Till derived from acid schist and basic igneous rocks.
◒ Insch Association. Till derived from basic igneous rocks.
● Countesswells Association. Fallen tree samples (1953 gale).

FIG. 1. Total air-space modal values for indurated layers developed on different parent materials.

the acid granitic till on which the Contesswells Association is developed is about 24–26 per cent.; whilst for the mixed acid/basic till on which the Tarves Association is developed, and the Lower Old Red Sandstone-derived till on which the Balrownie Association is developed, the figure is about 28–30 per cent. For the basic igneous till on which the Insch Association is developed the figure is about 34–36 per cent. air space. Recalling that the clay fraction of the indurated layer contains small amounts of translocated alumina in the absence of reactive iron oxide, it is perhaps significant that the parent material of the Insch Association contains a high proportion of actively weathering ferromagnesian minerals, whereas the visibly red colour of the Lower Old Red Sandstone-derived parent material of the Balrownie Association is due to geologically inherited iron oxides.

The dotted curve on the histogram (Fig. 1) has been prepared from data obtained by sampling indurated layers in the holes left by fallen trees after the great gale of 31 January 1953. The parent material is granitic till of the Countesswells Association. The modal value for the indurated layers developed in this material shows an increase from the normal 24–26 per cent. to 26–28 per cent., reflecting partial shattering of this relatively brittle layer by the thumping and rocking of the trees in the

gusting winds. A few determinations made on similar material from the Insch Association, though insufficient to be conclusive, showed no apparent rise in the modal value for this parent material. This suggests that the relatively higher total-air-space values for indurated layers developed on a basic parent material are accompanied by softer cementation.

Much less data are available on the weakly podzolized and brown forest soils of East Scotland and the Borders. In such profiles (Table 6) the indurated B_3 horizon is weakly developed or absent. There is an open porous structure near the surface that deteriorates gradually with depth. This is reflected in a more gradual drop in air space below the B_2 horizon.

TABLE 6

A Freely Drained Profile from Paddock Slack (Selkirkshire). Parent Material: Till derived from Silurian Shales and Greywackes

Depth from Surface	*Air space*
10–14 in.	Values between 40 and 58 per cent. recorded—samples were very fragile and tended to break up.
15–19 in.	$52{\cdot}1 \pm 1{\cdot}4\%$
24–28 in.	$39{\cdot}2 \pm 2{\cdot}5\%$

Imperfectly drained soils

In north-east and east Scotland the imperfectly drained soil covers the transition between the podzolic and gley soil groups. In other districts it may be a low-base-status brown forest soil with gleyed B and C horizons, depending on the local parent material and climatic conditions.

In podzolic profiles where the indurated layer is present there is much the same sequence of total air-space values as already noted for freely drained podzolic soils, except that where gleying is appreciable in the B_2 horizon the total air space may be nearer 40 than 50 per cent. Where induration is absent total pore space is usually within the range 35–40 per cent. in the B_2 horizon (as most of the soils in this group are under arable cultivation this is in practice the horizon immediately below the plough layer) with a gradual fall in total air space in successive underlying horizons to a depth of about 3 ft. This relation has been found to hold for soils whose individual parent materials may range in clay content between 20 and 60 per cent., and whose geographical range extends from Aberdeenshire to Roxburghshire (Table 8).

Poorly drained soils

The poorly drained soils discussed are all non-calcareous gleys. The general trend in these profiles is very similar to that developed in the weakly gleyed imperfectly drained soils. For cultivated soils, total air-space values usually range from 30 to 40 per cent. in the gley horizon below the plough layer, with a small but consistent drop in subsequent underlying horizons (Table 9). A reversal of this trend has been recorded for Foodie farm in Fifeshire (Table 9). This profile is a surface-water gley developed on till derived from andesitic lavas.

Uncultivated poorly drained soils reveal a similar trend to that of cultivated soils, when compared at equivalent horizon levels. But rather high total-air-space values have been recorded in the upper gley horizon of soils of the Ettrick Association in the Border country (Table 9). These are developed on a till derived from Silurian shales and greywackes containing a high percentage of silt and fine sand. Comparison, however, with a poorly drained cultivated soil of the rather similar Foudland Association of Aberdeenshire (Table 9) discourages speculation that this is a parent-material effect. The high values are probably more closely related to better soil structure and higher soil faunal activity under the semi-natural grassy vegetation with mull-moder humus in the Border country.

Very poorly drained soils

The very poorly drained soils which have been examined have a limited parent-material and geographical range. This is partially due to the difficulty of obtaining this series within a uniform hydrologic sequence, as it is most commonly developed in low-lying alluvial hollows and channels, thus frequently introducing a parent material discontinuity

The profiles for which total-air-space values are listed in Table 10 are from north-east Scotland and the Border country. Those from the north-east are developed on granitic till, and mixed tills derived from granite or acid schists with some basic igneous material; whilst in the Borders only one parent material is represented, a till derived from Silurian shales and greywackes. The usual gley-soil trend is followed with a small, or very small, gradual fall in total air space down the profile. The total-air-space values for the first gley horizon below the plough layer in north-east Scotland are generally within the range 28–34 per cent.; those for two profiles from the Borders show a range from 35 to 38 per cent. It is probable that diffuse organic matter in the first mineral horizon of these soils accounts for part of the rise as discussed above, but the behaviour does parallel that of the poorly drained peaty gley soils developed on the same parent material, and may be related.

Alluvial soils

Alluvial soils examined so far do not consistently follow any of the trends which have been described above for hydrologic sequences of soils developed on glacial tills.

The results for four alluvial profiles from Angus and Kincardineshire are listed in Table 11. Two are estuarine or lacustrine alluvium with moderate to high silt-plus-clay values throughout, and two are river terrace alluvium with moderate to low silt-plus-clay values. There seems to be a marked reluctance for total air space to fall appreciably below 40 per cent. over a very wide textural range. It has been noted that under grassland plant-rooting depth usually attains, and often exceeds, 40 in. on this type of material, as compared with a figure of about 30 in. or less for many other parent materials in the same district. The greatest depth of root penetration for parent materials other than alluvium usually coincides with a fall in total air space to 27 or 28 per cent.

Discussion

The air-space relationships within the hydrologic sequence as a whole and those of some of the individual profile types have been described. In general they reflect closely the influence of hydrologic environment on the development of soil structure.

In the freely drained podzolic soil with indurated layer the friable B_2 horizon is porous and retains an aerated condition throughout most of the year. The underlying indurated B_3 horizon is highly impermeable, so that the lower few inches of the B_2 horizon may be soaked with surface water for appreciable periods in the year, and may develop a cloddy structure. The full response to this condition is seen in the B_2 horizon of the imperfectly drained soil with indurated layer, where the development of a friable cloddy or cloddy structure is accompanied by a reduction in total air space from 50 to 40 per cent. and a decrease in the visible porosity of individual structural units. The development of gleying above the indurated layer implies that this layer was itself formed before the gleying took place. The soil pattern found in the Border country suggests that formation of the layer takes place at a relatively early stage in the development of the podzol profile. Freely drained brown forest soils with deep friable B horizons, like the profile from Paddock Slack in Table 6, can be seen to merge laterally into more strongly leached podzolic soils with some development of the indurated layer. The data presented in Fig. 1 are from north-east Scotland where the podzol profile with indurated layer is vigorously developed. The manner in which the degree of cementation is related to the type of parent material accords well with the chemical evidence presented by Glentworth (1954) of relative accumulation of alumina in the clay fraction of the indurated layer.

The 35–40 per cent. air space recorded in the upper subsoil horizon of the poorly drained gley soil reflects the development of prismatic structure with relatively massive individual structural units, in response to seasonal rise and fall of the water table. Air-space values within the profile of a ground-water gley soil fall as the base level of the soil water table is approached, and the prismatic structure dies out. The C-horizon value of about 30 per cent. for the poorly drained gley soil is approximately that found in the upper levels of the very poorly drained peaty gley soil. In the latter, under semi-natural conditions, an anaerobic regimen persists throughout the greater part of the year, and the profile has no structure.

REFERENCES

GLENTWORTH, R. 1954. The soils of the country round Banff, Huntly and Turriff. Mem. Soil Survey, Gt. Britain, pp. 135–6.

—— and DION, H. G. 1949. The association or hydrologic sequence in certain soils of the podzolic zone of north-east Scotland. J. Soil Sci. **1**, 35–49.

RUSSELL, E. W., and BALCEREK, W. 1944. The determination of the volume and air space of soil clods. J. Agric. Sci. **34**, 123–32.

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Soil Associations listed in Tables 7 to 11

Association Name	*Parent Material*
Insch	Till derived from basic igneous rocks.
Tarves	Till derived from acid schists and basic igneous rocks.
Strichen	Till derived from acid schists.
Foudland	Till derived mainly from andalusite schists.
Countesswells	Till derived from granite and granitic gneiss.
Balrownie	Modified till derived from Lower Old Red Sandstone rocks.
Turin	Till derived from flaggy and shaly beds of L.O.R.S. age.
Strathfinella	Till from sandstone and conglomerate of L.O.R.S. age.
Mountboy	Modified till derived from L.O.R.S. strata and lavas.
Sourhope	Till derived from andesitic lavas.
Ettrick	Till derived from Silurian shales and greywackes.
Whitsome	Till derived from Lower Carboniferous sandstones, limestones, shales, and basalts, with some Upper O.R.S. sediments and Silurian greywackes.
Ashgrove	Till derived from Coal Measure shales and sandstones.
Glenpark	Till derived from Calciferous Sandstone sediments.
Glenalmond	Till derived from L.O.R.S.

TABLE 7

Freely Drained Soils

Profile site		*Association*	*% total air space at different levels in the profile (depths in inches)*							
Greenhall farm	Aberdeenshire	Insch (c)	10–13	50·8±0·5	17–20	35·5±0·9	27–30	33·5±0·5	38–41	34·0±0·4
Harthill farm	Aberdeenshire	Insch (c)	12–16	49·0±2·3	17–21	31·5±0·5	20–24	32·7±0·7	37–41	26·2±0·4
White Caterthun	Angus	Strathfinella	7–11	58·6±0·4	23–27	32·2±0·3	34–37	32·8±0·5		..
Parkhead farm	Aberdeenshire	Countesswells (c)	9–12	53·3±1·1	13–17	22·5±0·6	21–25	24·2±0·7	28–32	23·7±0·1
Glentannar	Aberdeenshire	Countesswells	8–11	57·2±1·4	20–23	27·2±0·9		..		..
Alten farm	Aberdeenshire	Tarves (c)	9–11	53·8±0·4	13–17	27·7±0·6	19–21	43·7±1·2		..
Pitterie hill	Angus	Mouatboy (c)	8–11	52·4±0·9	15–17	40·6±1·3	17–21	33·1±0·9	22–27	29·9±0·6
Balcalk farm	Angus	Turin (c)	11–15	52·7±0·5	18–22	39·9±0·9	24–26	37·5±1·8	26–28	37·4±0·4
Sourhope farm	Roxburghshire	Sourhope (c)	10–13	45·7±0·7	13–16*	41·9±0·9		..		..
Foodie farm	Fife	Sourhope (c)		..	13–16	33·9±0·8	16–21	34·0±0·9	24–28	38·6±0·4
Andet farm	Aberdeenshire	Foudland (c)	11–14	49·7±1·1	20–24	27·4±0·4		..		..
Duthris hill	Angus	Strichen	8–11	55·1±1·0	19–23	29·9±0·7		..		..
Anniegathel	Angus	Strichen	9–13	49·9±1·2	27–30	28·8±0·5	34–38	32·0±0·4		..
Broom farm	Angus	Balrownie (c)	9–11	45·7±2·4	14–16	31·6±0·5	29–32	28·1±0·6		..
Wood of Aldbar farm	Angus	Balrownie (c)	11–14	49·4±0·6	23–26	32·9±0·6	35–38	33·3±0·9		..

* No indurated layer present. All the other figures in this column refer to indurated B_2 horizons. (c) Cultivated soil.

TABLE 8

Imperfectly Drained Soils

Profile site		*Association*	*% total air space at different levels in the profile (depths in inches)*									
Little Swinton farm	Berwickshire	Whitsome (c)	8–12	33·6±0·8	12–16	32·2±0·5	16–19	28·0±0·5	28–32	25·8±0·8	..	
Third Lowhaugh farm	Berwickshire	Whitsome (c)	15–19	34·8±0·2	22–26	32·7±0·2	29–32	30·6±0·2	33–36	30·4±0·2	36–39	30·7±0·2
Sourhope farm	Roxburghshire	Sourhope (c)	10–13	41·9±0·8	14–16	35·5±0·4	27–30	36·1±0·3		..		..
Foodie farm	Fife	Sourhope (c)	11–15	39·7±0·5	18–22	37·5±0·9		..		..		..
Derachy farm	Angus	Balrownie (c)		..	15–18•	28·4±0·5	22–26	29·9±0·4		..		..
Montreathmont moor	Angus	Balrownie	5–8	53·0±1·1	15–18•	27·4±0·7	23–26	27·6±0·6	38–41	28·1±0·3		..
Forest moor	Angus	Balrownie	13–15	59·7±1·3	17–21•	32·4±0·8	22–24	30·1±0·9	30–33	28·2±0·7	37–41	29·4±0·4
Newton of Inshewan farm	Angus	Balrownie (c)	10–14	37·3±1·6	14–17	31·5±1·3	26–30	28·9±0·3	35–37	29·4±0·2		..
South Leckaway farm	Angus	Balrownie (c)	10–13	46·3±0·4	14–17	38·4±0·9	17–20	39·5±1·6	24–26	31·1±0·4	37–40	30·1±0·4
Bonnyton farm	Angus	Balrownie (c)	9–12	34·8±0·2	13–16	32·2±0·4	21–24	29·7±0·8	30–33	28·4±0·5		..

• Indurated B_2 horizons. (c) Cultivated soil.

TABLE 9

Poorly Drained Soils

Profile site		*Association*	*% total air space at different levels in the profile (depths in inches)*							
Greenhall farm	Aberdeenshire	Insch (c)	10–13	39·4±0·7	18–21	36·7±0·5	28–31	35·2±0·7	..	
Harthill farm	Aberdeenshire	Insch (c)	12–16	36·5±0·8	22–27	34·2±0·3	31–36	31·0±0·4	..	
Millhill farm	Aberdeenshire	Tarves (c)	11–15	32·1±0·5	20–24	29·7±0·3	30–34	29·3±0·2	..	
Hill of Nathro	Angus	Strichen (c)	12–14	36·1±0·8	16–20	31·6±0·8	35–39	31·6±0·6	44–48	28·0±0·6
Anniegathel	Angus	Strichen	9–12	35·7±1·1	19–23	32·5±0·4	30–33	28·4±0·8	..	
Bettywharren	Angus	Strichen	10–14	48·2±0·7	16–19	38·7±0·3	23–27	37·2±0·6	..	
Sourhope farm	Roxburghshire	Sourhope (c)	8–11	37·5±0·3	16–19	34·9±0·4	27–30	34·5±0·3	..	
Foodie farm	Fife	Sourhope (c)	10–14	35·4±0·9	14–17	37·5±1·0	17–21	40·7±0·4	..	
Braston farm	Ayrshire	Ashgrove (c)	12–18	33·4±0·4	21–26	31·3±0·6	..		..	
Little Swinton farm	Berwickshire	Whitsome (c)	10–14	33·7±0·4	18–21	28·7±0·2	28–32	25·6±0·4	34–37	25·1±0·3
Forest moor	Angus	Balrownie	10–13	38·6±0·5	17–20	31·9±0·3	23–27	29·0±0·8	..	
Eddieston farm	Aberdeenshire	Countesswells (c)	13–18	29·3±1·1	24–27	25·4±0·6	..		..	
Paddock Slack	Selkirkshire	Ettrick	10–13	43·7±0·8	17–20	29·1±0·8	28–31	27·7±0·4	..	
Paddock Slack	Selkirkshire	Ettrick*	10–13	47·5±1·5	17–20	38·9±0·9	28–31	26·3±0·8	..	
Andet farm	Aberdeenshire	Foudland (c)	11–14	32·7±1·4	21–25	32·5±0·5	30–34	22·3±2·7	40–44	36·1±0·5

* Poorly drained peaty gley soil. (c) Cultivated soil.

TABLE 10

Very Poorly Drained Soils

Profile site		*Association*	*% total air space at different levels in the profile (depths in inches)*							
Millhill farm	Aberdeenshire	Tarves (c)	12–16	33·7±0·8	18–22	30·4±0·8	25–29	28·2±0·3	33–37	27·0±0·4
Tillycorthie farm	Aberdeenshire	Tarves (c)•	8–11	30·5±0·1	14–17	29·9±0·1	20–23	30·0±0·1	30–33	29·4±0·3
Tillycorthie farm	Aberdeenshire	Tarves (c)	11–14	32·1±0·9	17–20	29·2±0·3	24–27	27·0±0·1		..
Alten farm	Aberdeenshire	Tarves (c)	10–15	31·6±0·6		..	28–33	28·9±0·5		..
Woodburn	Roxburghshire	Ettrick	9–12	35·6±1·0	15–18	37·7±0·2	26–29	29·2±0·2		..
Wiggburn	Roxburghshire	Ettrick	11–14	38·1±0·7	15–18	36·4±0·4		..		..
Parkhead farm	Aberdeenshire	Countesswells (c)	11–14	27·8±0·5		..		..		..
Milton farm, Tarfside	Angus	Strichen	14–18	29·4±0·6		..		..		..

• 'Improved' very poorly drained soil. (c) Cultivated soil.

TABLE 11

Alluvial Soils

Profile site		*% total air space at different levels in the profile (depths in inches)*									
Powis farm	Angus (c)	10–14	39·9±0·4	19–23	41·0±0·3	31–35	43·7±0·1	42–45	46·0±0·2	51–55	46·3±0·1
West Ingliston farm	Angus (c)	10–14	41·5±0·1	20–24	45·6±0·7	26–30	49·9±0·8	31–33	38·9±0·2	36–39	42·2±0·5
Balmakewan farm	Kincardineshire (c)	10–13	41·4±0·4	18–21	48·2±0·4	25–28	53·5±0·4	35–38	52·4±0·3		..
Birkenbush	Angus (c)	9–12	45·5±0·1	15–18	44·2±0·4	20–23	41·9±0·1	26–29	42·0±0·1		..

(c) Cultivated soil.

A MODIFIED PERMEABILITY TEST FOR MEASURING THE COHESION OF SOIL CRUMBS

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Summary

The technique previously described (Emerson, *J. Soil Sci.*, **6**, 160, 1955) has been improved. A 1-cm. thickness of soil crumbs of standard size (1–2 mm. diameter) is supported on a 1-cm. layer of glass spheres (0·5–1 mm. diameter), and the permeability measured by percolation of 0·05 N NaCl—the so-called 'initial' test. Then 3 litres of the same solution are percolated in 24 hours, after which the permeability measurement is repeated—the 'final' test. The ratio, K_2/K_1, of final and initial permeabilities of the crumbs is regarded as a measure of soil cohesion.

The technique has been applied to a wide range of soils, on some of which other structural tests had already been made. The results, in four tables, show: (*a*) a continuous arable system produces very bad structure; (*b*) a short-term ley produces an improvement—as does wheat—and some of the improvement is detectable after a subsequent year in arable cultivation; (*c*) attainment of maximum stability is very slow, for 100 years in grass may not be enough; (*d*) farmyard-manure residues increased crumb stability on a clay soil, but not on a sand; (*e*) a ley, and lucerne too, produces a greater increase than root crops.

Limitations of the test are: (*a*) It should not be used unless the soil acidity is approximately the same for all samples. Very acid clay (pH 4 to 5), known to possess a very poor structure, gives a value of K_2/K_1 close to unity. (*b*) It may not be safe to compare soils of differing clay content. A poorly structured sandy loam (12 per cent. clay) gives a much higher value of K_2/K_1 than a clay loam (31 per cent. clay) that field experience would assess as having the better structure.

1. *Introduction*

EMERSON (1954, 1955) described a method of estimating the cohesion of moist soil crumbs in which he sought a limiting dilution of sodium chloride at which a bed of crumbs became impermeable because of deflocculation of the clay. The exchange complex in the soil was first saturated with sodium, and then a bed of crumbs of standard size was brought into equilibrium with successively more dilute solutions of sodium chloride, the permeability being measured at each stage. For soils with good structure, the permeability did not fall to zero even in distilled water, but weaker soils dispersed before this end-point, and there were occasions when the dispersed material passed through into the pores of the supporting sintered glass. Results from such soils were erratic for this reason alone, but there were other sources of non-reproducible behaviour, such as the changes in density and viscosity of the percolating solutions.

The modified technique of the present paper employs a single concentration of electrolyte throughout, so eliminating the need for density and viscosity corrections, the value chosen being sufficiently high to avoid any important deflocculation of any soil, and sufficiently low to

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produce a marked decrease in permeability in soils known from field behaviour to possess 'poor structure'. A more open support for the crumb bed does not become blocked by any dispersed clay that may reach it. In combination, the modifications have made the test less tedious and more reproducible.

2. *The Apparatus* (*Fig. 1*)

(*a*) *The permeameter* (*P*)

The upper part, 6 cm. long, has an inside diameter of 2·54 cm. Below, it tapers to an inner diameter of 0·5 cm. in a section about 9 cm. long. Above the taper rests a disc of wire gauze with holes less than 0·05 cm.

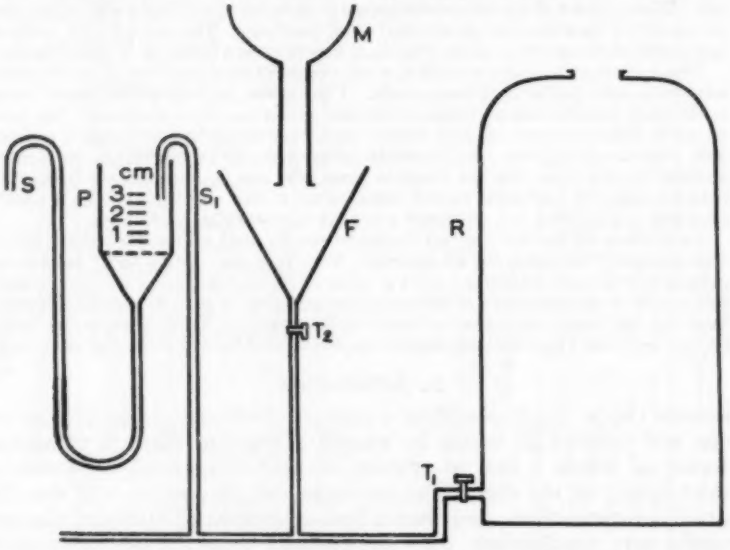

FIG. 1.

diameter, and at this level on the glass is the zero mark of an engraved scale 0–3·0 cm. by millimetres. The stem of the funnel is connected to a siphon tube, *S* (0·5 cm. diameter), which can be set in a position relative to *P* as shown in the diagram.

To set up the permeameter, it is first filled with electrolyte (0·05 N NaCl), and then 8·8 g. of glass spheres (0·5 to 1·0 mm. diameter) are poured in. After gentle tamping these settle down to form a layer 1·0 cm. thick, free from air bubbles. The side limb, *S*, is then lowered until the liquid level in it is 8 cm. below the level of the top of the spheres (7 cm. below the gauze). The air-dry soil crumbs are now poured onto the top of the glass spheres until the crumb bed is 1 cm. thick (measured on the engraved scale). As the soil wets slowly the suction is maintained at 8 cm. by raising, or by topping-up, the side arm. When uptake is complete the side arm is raised until the electrolyte in it stands at 1·0 cm.

above the top of the crumbs. The siphon path is now completed with the syphon outlet at this same level, and the siphon is then clamped in place.

Two sources of supply of electrolyte are needed but both reach the permeameter by the siphon tube S_1.

(*b*) *Timing reservoir* (*R*)

This is the source of the hydraulic head, and is a large jar with a cross-sectional area of 335 cm.^{2} (A_1 in para. 3). It is set on a firm support so that the liquid level in it is normally a few millimetres above the outlet of *S*: with tap T_1 left open, its equilibrium level will be the same as that of the liquid in *P*. The reservoir is only in use during permeability measurements before and after the flushing process, during which T_1 is kept closed.

(*c*) *Flushing reservoir* (*M and F*)

The arrangement shown in the middle of the figure is used to provide a slow flow of electrolyte through the soil over a long period. Precise control of rate is not essential, and an ordinary glass tap at T_2 is adequate after the coarse adjustment of the level of the inverted flask (*M*) containing the electrolyte (0·05 N NaCl) over the funnel *F*. (The usual rate is 3 litres in 24 hours.)

(*d*) *Blank unit* (*not shown*)

Several units such as *P* can be fed in parallel from the same supply line, and by suitably placed taps (not indicated) any or all of them can be used simultaneously. Six are normally used, one of which contains no soil and is employed as a control unit to ensure that the liquid level in *R* during the 'final' permeability measurement is the same as it was a day earlier during the initial measurement.

(*e*) *Operation*

With the permeameter set up as in (*a*), and with T_2 and T_1 closed, the electrolyte (0·05 N NaCl) level in *R* is set at about 3 mm. above that of the outlet of *S*. To start, T_1 is opened, and the discharge from *S* collected *as drops* in a 10 cm.^{3} graduated cylinder. The first cm.^{3} is ignored and the stop-watch is started when the discharge has reached 1·0 cm.^{3}, and stopped when 10·0 cm.^{3} have been collected. The discharge is returned to *R*, and the operation repeated. At least three consecutive reproducible times, not differing by more than 0·2 sec. (in about 35), are obtained. The mean of these gives the time t_1 for use in equations 2, 3, and 4.

Similar replicate runs are made on the blank to give a percolation time, say t_0 (it does not appear in any of the equations).

Tap T_1 is then closed, and T_2 is opened, under control, to permit 3 litres of electrolyte to pass through *P* in about 24 hours. Depending on their cohesion, the crumbs may break down, and the clay may swell: changes of 33 per cent. of initial thickness may occur, and the new dimension (z_2 in equations 3 and 4) is read on the graduated scale.

Now tap T_2 is closed, and the timing reservoir R brought into circuit. The first permeability test is on the blank permeameter. If the time for 9 ml. is not within 0·2 sec. of t_0 the level of liquid in R is adjusted until this condition is satisfied. When it is, it is assumed that every permeameter now has exactly the same head for its 'final' test as it had for the initial test. The mean time (t_2 in equations 3 and 4) is now measured for each of them, and the index of cohesion calculated from the ratio of final/initial permeability:

$$\frac{K_2}{K_1} = \frac{t_1 z_2}{t_2 z_1 + (t_2 - t_1) z_s K_1/K_s}, \tag{4}$$

in which $t_1$and t_2 are measured times,

z_2 is the final thickness of soil bed,

$z_1 = 1{\cdot}0$ cm.,

$z_s = 1{\cdot}0$ cm. (thickness of bed of glass spheres),

K_1 = initial permeability of crumbs,

= 1·26 cm. water/sec. (see para. 4 (*a*)),

K_s = permeability of bed of glass spheres,

= 0·215 cm. water/sec. (see para. 4 (*a*)).

(*f*) *Sensitivity*

Before giving the theoretical derivation of the equation, and an account of the work done to measure the constants and decide on best values of the controllable variables, typical values can be given, taking the easy case of $z_2 = z_1 = 1{\cdot}0$ cm. (i.e. no swelling). For an initial head near 0·30 cm., $t_1 = 34{\cdot}0$ sec., and the expression reduces to

$$K_2/K_1 = 34/(6{\cdot}87t_2 - 200),$$

and from this Table 1 is obtained:

TABLE 1

Dependence of Permeability Change on Measured Time

t_2 (*sec.*)	K_2/K_1 (%)	t_2 (*sec.*)	K_2/K_1 (%)
34·0	100	36·0	72
34·25	94	38·0	56
34·50	92	42·0	39
35·00	85	46·0	29

3. *Theoretical*

It is assumed that the Darcy equation can be applied to a bed of soil crumbs, and to the support on which it rests. In the steady state, this takes the form

$$Q/t = KAh/z, \tag{1}$$

where Q/t is the volume flowing in unit time (cm.^{3} sec.$^{-1}$),

K is the permeability (cm. water sec.$^{-1}$),

A is the area of cross-section normal to the direction of flow (cm.^{2}),

h is the hydraulic head (cm. water),

z is the thickness of the layer (cm.).

If soil of permeability K_1, thickness z_1, rests on a support of permeability K_s, thickness z_s, and the pressure drops are respectively h_1 and h_s, then if h is the total pressure drop

$$h = h_1 + h_s,$$

$$Q/At_1 = K_1 h_1/z_1 = K_s h_s/z_s,$$

or

$$h = \frac{Q}{At_1}\left(\frac{z_s}{K_s}+\frac{z_1}{K_1}\right). \tag{2}$$

If after treatment the supported material changes its permeability to K_2, and swells to thickness z_2, and the same volume of water now takes t_2 sec. to pass through, under the same total head, then

$$h = \frac{Q}{At_2}\left(\frac{z_s}{K_s}+\frac{z_2}{K_2}\right).$$

If the head can be precisely controlled and measured, then the properties of the support can be eliminated (presuming them invariant) to give

$$\frac{K_2}{K_1} = \frac{z_2}{z_1 + hAK_1(t_2-t_1)/Q}. \tag{3}$$

In practice neither the setting nor the measurement of the head can be made accurately enough and it is better to use equation 2 to estimate the head. The ratio of the permeabilities is then

$$\frac{K_2}{K_1} = \frac{t_1 z_2}{t_2 z_1 + (t_2-t_1) z_s K_1/K_s}. \tag{4}$$

The ratio, K_2/K_1, is to be used as an index of cohesion, and equation 4 reveals that it depends on the absolute values of K_1 and K_s. It is assumed that K_1 is a constant for all soils, being dependent only on the crumb size, and all crumbs are selected in the same way (1·0–2·0 mm. diameter range). Possible variation in K_1 will be of little importance if z_1 can be made very much greater than z_s, or if K_s can be made large. Unfortunately the depth of soil, z_1, cannot be increased much above the 1 cm. used, as the bottom layer of very weak soils is crushed by the overburden, and the initial permeability is thereby reduced much below the value K_1. Increase in K_s is desirable on physical grounds, because the large pores needed are less liable to be blocked by dispersed clay. This blocking was one of the major disadvantages of the original technique, and its avoidance is the main reason for the modifications now being described. Still short of the pore size at which the crumbs themselves would fall through there is, however, an upper limit acceptable in practice. It is necessary to wet the crumbs slowly under tension to avoid

breakdown, and to meet the requirement the pores in the support should be capable of withstanding a suction of 8 cm. of water. The choice of glass spheres in the diameter range 0·5 to 1·0 mm. has proved adequate. Experiments to measure K_1 and K_s are described in paragraph 4 (*a*).

In the derivation of equations 3 and 4 there is the implicit assumption that the head is constant. This is not true, as the level in the reservoir (Fig. 1) falls as the Q cm.^{3} of water are withdrawn. If the initial head (at $t = 0$) is h_0, and the area of cross-section of the reservoir is A_1 cm.^{2}, then the fall in head is Q/A_1 cm. If this quantity is small compared with h (in practice it is about $h/10$) then second and higher order terms in Q/Ah can be neglected, and it is easy to show that equation 3 is exact if h is read as the arithmetic mean of the initial and final heads, i.e. $h = h_0 - Q/2A_1$. As A_1 is a geometrical constant, and Q is fixed as an operational constant, h is uniquely determined by h_0.

4. *Experiments to Guide Permeameter Design*

(*a*) *Permeability of glass spheres and soil crumbs* (K_s *and* K_1)

Values of K_s and K_1 were measured in the same way. The glass spheres were selected in the diameter range 0·5 to 1·0 mm. The soil crumbs, prototype of all others, were the sieved 1 to 2 mm. fraction of air-dry crumbs from Hoosfield on the Rothamsted farm. To avoid breakdown on flooding they were first wetted slowly at 50 cm. water suction before being tipped into a permeameter.

For this test the soil was supported on a fine mesh wire gauze (no layer of glass spheres) and a column 3 cm. high formed. Distilled water was used as percolating liquid, and in the first run the head between R and S (Fig. 1) was only known approximately. Rates of discharge were then measured for different settings of S, keeping the liquid level in R constant. The results appear in Fig. 2 where the abscissa is the change in the position of S. From equation 1 the slope of the line is KA/z and as $A = 5{\cdot}05$ cm.^{2} and $z = 3{\cdot}0$ cm., the derived values of K are

K_s (0·5–1·0 spheres) = 0·215 cm. water/sec.
K_1 (1·0–2·0 crumbs) = 1·26 „ „

Experiments with sand in the same size range as the spheres gave the same mean value of permeability, but with a greater scatter.

(*b*) *Choice of electrolyte concentration*

Three test soils were used, ranging from very poor structure to moderately good. Air-dry crumbs (1–2 mm.) were sodium-saturated with 0·5 N NaCl and then normal permeability measurements made using five concentrations of electrolyte between 0·04 and 0·10 N NaCl. The results are in Fig. 3. Almost any concentration in this range will permit discrimination between the soils. The choice of 0·05 N is arbitrary, but it does show the poorest soil known to us as having minimum cohesion.

(*c*) *Volumes and rates in flushing*

Most English soils are calcium-saturated, and many of the Rothamsted fields have free calcium carbonate in the surface layers. In the

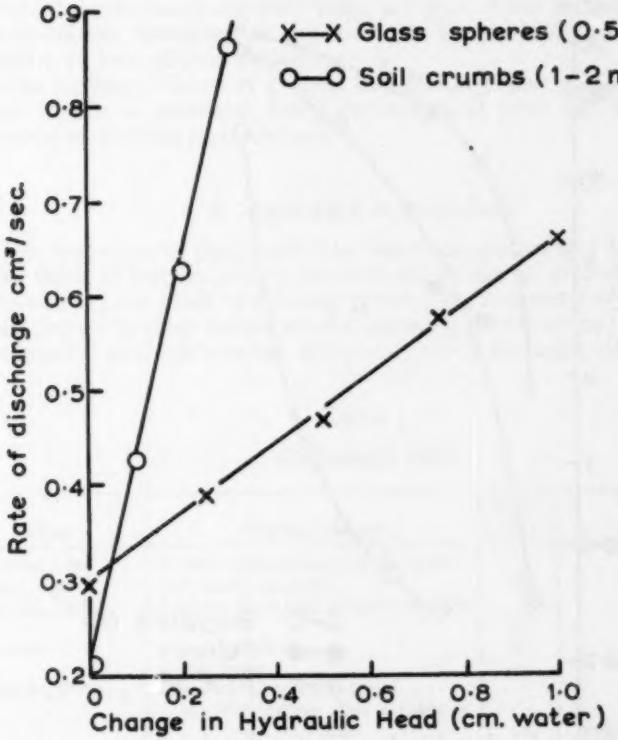

FIG. 2.

process of sodium saturation the rate of exchange of Ca^{++} by Na^{+} depends on the rate of diffusion of Ca^{++} from the crumbs, i.e. on the concentrations of Na^{+} and Ca^{++} in the percolating solution (Quirk, 1952). To obtain complete replacement the concentration of Na^{+} in the percolating solution should be as high as possible, but as this has already been fixed, the control must be by volume and rate.

The choice was made empirically, the test soil being the weakest available—Barnfield 80. Standard technique (para. 2(*e*)) was used but with different total volumes of 0·05 N NaCl for different periods of time. The concentration of Ca^{++} in the first 30 ml. of percolate, and that in equilibrium with the crumbs after 24 hours of percolation, were determined by versenate titration. The results of permeability measurements are in Table 2. The final permeability depends on the volume of percolate (upper group) but is independent of the time in the range examined.

After correcting for the contribution of Ca^{++} from the free calcium carbonate, the first 30 ml. of percolate carried away 0·5 m.e. of Ca^{++}, the

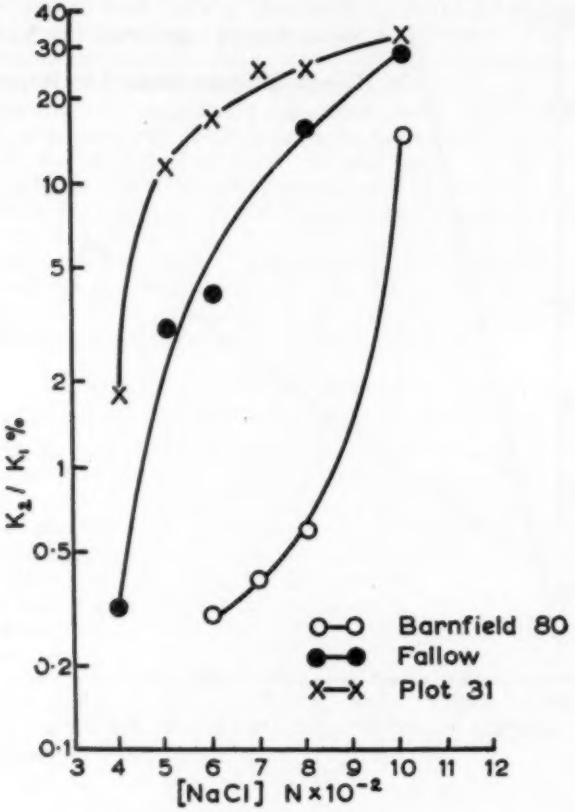

FIG. 3.

TABLE 2

Dependence of Permeability on Amounts and Times of Flushing

Volume of 0·05 N NaCl percolated (cm.³)	*Time (hr.)*	K_2/K_1 (%)
3,000 { 800 + 600 + 600 } 2,000 + 1,000	96 { 24 + 24 + 24 } 72 + 24	33 ↓ 23 ↓ 13 ↓ 5
2,000	24	13
3,000	24	5

known base exchange capacity being 0·6 m.e. After 24 hours the Ca^{++} concentration decreased to 0·3 m.e. per litre, which is attributed to solution of free calcium carbonate.

The flushing volume of 3 litres, and flushing time of 24 hours, have been chosen as standard, being convenient in scale and adequate for removal of calcium from the soil.

5. *Application to Field Soils*

The technique of paragraph 2 (*e*) has been applied to a range of soils from fields of known history, some of which can be graded in terms of structure on the basis of farming experience, and some of which have been graded by other techniques for assessing soil structure (Tables 3–6). Mechanical analyses of some of the soils are in the appendix.

TABLE 3

Rothamsted Soils

Source	*Previous history*	K_2/K_1 (%)	*Remarks*
Barnfield 8o	Arable: unmanured for 82 years	5	..
Highfield	Permanent pasture	87	..
Barnfield 2AC	Arable: farmyard manure for 82 years	18	..
Fosters	4-year fallow	18	..
	4-year grass	50	..
Broadbalk Plot 3	Unmanured for 119 years		
	(*a*) Bare fallow after 4 years of winter wheat	18	Sampled in spring
	(*b*) 4th-year wheat after 1 year bare fallow	43	..
Broadbalk Plot 2	Farmyard manure for 106 years		
	(*a*) As above	31	..
	(*b*) As above	56	..

TABLE 4

Jealott's Hill Soils (*Data other than* K_2/K_1 *kindly supplied by A. J. Low*)

Source	*Previous history*	K_2/K_1 (%)	*Water-stable aggregates*
			>2 mm.%
JH 18 1 IV	100 years' grass	90	68
JH 21 1 III	Continuous arable	35	33
			>0·5 mm.%
A_2 Plot 33	Wheat, barley, ley, kale	43	3·8
34	Wheat, barley, barley, kale	38	0·7
45	Ley, ley, ley, kale	66	10·0
46	Wheat, ley, ley, kale	60	6·7

TABLE 5

John Innes Soils (Data other than K_2/K_1 kindly supplied by N. W. Alvey)

Source	*Previous history*	K_2/K_1 (%)
L 7	1st-year ley after arable fallow	4
L 7	2nd-year ley after arable fallow	8
L 8	1st-year ley after ryegrass	5
L 8	2nd-year ley after ryegrass	54
M II 28	1st-year ley after fallow	25
M II 16	2nd-year ley after fallow	39
H I 28	1st-year ley after fallow	20
H I 8	2nd-year ley after fallow	52

TABLE 6

Woburn, Ley/Arable, Soil

Source	*Previous history*	K_2/K_1 (%)	*Depth (in.)*
Plot 58	Unmanured: 3rd-year ley (grazed)	62	0–2
		50	2–4
„ 57	Farmyard manure: 3rd-year ley (grazed)	66	0–2
		51	2–4
„ 60	Unmanured: 3rd-year lucerne (cut for hay)	64	0–2
		63	2–4
„ 59	Farmyard manure: 3rd-year lucerne (cut for hay)	64	0–2
		39	2–4
„ 64	Unmanured: potatoes, rye, sugar beet	44	0–2
		42	2–4
„ 63	Farmyard manure: potatoes, rye, sugar beet	26	0–2
		33	2–4
Headland	Clean cultivated headland	14	0–2
		15	2–4

It may be concluded from these results that:

(*a*) A continuous arable system produces very bad structure, e.g. Barnfield 80 (Table 3) and Woburn headland (Table 6).

(*b*) A short-term ley produces an appreciable improvement, e.g. Fosters (Table 3), the A_2 soils (Table 4), the L, M, and H soils (Table 5), and Plots 57 and 58 (Table 6). Some of this improvement persists after a year in arable cropping (Table 4). An improvement has occurred very rapidly with a wheat crop, e.g. Broadbalk Plots 2 and 3 (Table 3).

(*c*) Even 100 years in grass has failed to produce 100 per cent. permeability, as shown by the sodium-saturation method, and it may be inferred that the attainment of maximum stability is a very slow process, e.g. Highfield permanent pasture (Table 3) and JH 1 IV (Table 4).

(*d*) Organic matter residues (farmyard manure) increased crumb cohesion of the clay soils of Broadbalk, Plot 2, and Barnfield, Plot 2AC (Table 3), and the effect was not masked when the Broadbalk plots were cropped. Farmyard manure did not produce an appreciable increase in crumb cohesion of the sandy Woburn soil (Table 6).

(*e*) A ley and lucerne produce a greater increase in crumb cohesion than root crops (Table 6).

6. *Discussion*

A laboratory test such as this should satisfy certain requirements, some essential, and some desirable. First, it ought to be reproducible, and the main changes made in the technique have achieved this object, within acceptable limits. Second, it ought to be easy to use, but as yet this is not quite so. Third, the results obtained should be capable of interpretation; and, fourth, it should have some range of application to field soils. At present the interpretation of the results obtained is largely a reflection of field experience and intuition, in that the figures do put soils in an expected order of stability, e.g. soil from old grassland is more stable than similar soil subjected to long arable cropping. Where a parallel test has been made, the sodium method tends to put samples in the same order as the wet sieving test.

There are two properties of soil that limit the range of application of the test, namely acidity and clay content.

Measurements on soils from three Rothamsted fields with a long history of arable cultivation gave the results of Table 7.

TABLE 7

Permeability and pH

Soil	*pH in 0·01 M* $CaCl_2$	K_2/K_1 (%)
Barnfield 80	7·2	5
Hoos Exhaustion . . .	5·3	90
Broadbalk headland . .	3·7	100

The extreme range can hardly be an indication of structural differences. Attempts to buffer the soil, using half-neutralized para-nitrophenol have not been entirely satisfactory, and until a suitable buffer is found comparison of soils at markedly different pH should be avoided.

The limitation imposed by the clay content of the soil is illustrated by two extreme soils shown in Table 8. Each has been under arable cultivation for many years and both have poor structure in the field.

TABLE 8

Permeability and Clay Content

Soil	*% Clay*	K_2/K_1 (%)
Barnfield 80 . . .	31	5
Woburn soil . . .	12	51

The relatively high stability of the Woburn soil compared with that of Barnfield 80, as shown by the sodium test, is unlikely to be a fair comparison of the wet strength of these soils, but soils containing 20–30 per

cent. clay may be safely compared. The test can be applied to sandy soils when a comparison between the arable soil and soil after cropping or manurial treatment is required (see Table 6).

Acknowledgements

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REFERENCES

EMERSON, W. W. 1954*a*. The determination of the stability of soil crumbs. J. Soil Sci., **5**, 233.

—— 1954*b*. The effect of various grasses and lucerne on the cohesion of soil crumbs. Trans. Fifth Internat. Congr. Soil Sci., **11**, 65.

—— 1955. A note on the sodium saturation test for determining the cohesion of moist soil crumbs. J. Soil Sci., **6**, 160.

QUIRK, J. P. 1952. The deflocculation of soil colloids. Ph.D. thesis of the University of London.

APPENDIX

Mechanical Analysis of Some of the Soils Used

Soil	*Coarse sand*	*Fine sand*	*Silt*	*Clay*	*Carbonates*	*pH in 0·01 M* $CaCl_2$
I. Rothamsted						
Barnfield . .	6	37	21	29	0·5	7·2
Broadbalk . .	6	41	25	19	0·8	7·2
Fosters . . .	8	43	24	18	0·7	7·5
II. Jealott's Hill (Bracknell)						
J.H. 18 . . .	11	23	37	29	—	6·7
J.H. 21 . . .	11	20	32	37	+	7·2
A_2 . . .	45	30	10	15	..	..
III. John Innes (Bayfordbury)						
L	25	30	12	18	6	7·2
M	8	49	14	21	—	5·7
H	12	35	17	29	1	7·0

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THE EFFECT OF ORGANIC MATTER ON CRUMB STRUCTURE

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Summary

Tests made on soil crumbs from nearby long-term arable and grassland fields have shown that (*a*) the rate of water uptake of dry crumbs at 98 per cent. relative humidity was the same for arable and grassland crumbs and also grassland crumbs pretreated with H_2O_2; (*b*) the degree of swelling of dry arable and grassland crumbs in water is the same. It is concluded that the crystalline swelling of the clay in soil crumbs is unaffected by the soil having been under grass. No difference could be observed in the general arrangement of the quartz and orientated clay in thin sections of arable and the corresponding grassland crumbs.

From slaking and dispersion tests made on the natural crumbs and on remoulded crumbs formed by drying from a paste of the natural crumbs it is inferred that remoulding does not disperse the clay in either the grassland or arable crumbs, but does break-up many of the aggregates between 50 μ and 2 μ diameter in the grassland crumbs. The natural arable crumbs were so weak that immersion wetting of the dry crumbs was sufficient in itself to cause this break-up.

1. *Introduction*

THE strength of a soil crumb in water will depend on the number and nature of the bonds linking together the various constituents, such as the clay and the sand. Two main methods have been used to demonstrate the increased wet strength of crumbs following a ley. These are wet-sieving tests introduced by Tiulin (1928), which measure the breakdown of soil crumbs on wetting (slaking), and dispersion tests, introduced by Puri and Keen (1925), which not only measure the slaking of the crumbs but also the further dispersion of the wetted crumbs caused by end-over-end shaking. A review of the very extensive work using these techniques is given by Baver (1956). More recently the wet strength of crumbs has been measured by the resistance to dispersion of the crumbs after sodium saturation (Emerson, 1954; Dettmann and Emerson, 1959).

This paper describes further tests which have been made comparing soil crumbs from arable and pasture fields of similar mineralogical composition, with the aim of obtaining a model of a soil crumb that would explain the effect of soil organic matter on crumb stability. The tests have included measurement of the rate of water uptake, swelling and dispersion of the crumbs, and the examination of thin sections of the soils.

2. *Experimental Materials*

Illite

The separated clay fraction of Willalooka subsoil, supplied by C.S.I.R.O. Australia. X-ray analysis indicates that the fraction $< 2\,\mu$ is 85 per cent. illite and 15 per cent. kaolin. The clay was washed with N NaCl+0·001 N HCl to remove exchangeable Al^{3+} (Schofield and

Samson, 1954), followed by a strong solution of the appropriate chloride and finally dialysed in cellophane bags against water until chloride-free.

Soils

0–4 in. samples from:

Barnfield (Plot 80)	A calcareous clay soil from the Rothamsted farm, which has been under arable cultivation and unmanured for eighty years. The clay minerals present are mica types (60 per cent.), kaolinite (40 per cent.), and a little vermiculite.
Highfield	A calcareous clay soil from the Rothamsted farm, that has been down to grass for at least two centuries. This soil is mineralogically similar to Barnfield.
Hoos Ley	Soil from the Rothamsted Hoosfield (pH 6·2 in 0·01 M $CaCl_2$) which has been in grass ley for two years. Clay minerals as for Barnfield.
Weston Turville	Arable and permanent grassland calcareous clay soils from near Aylesbury, England. The clay fraction is predominantly montmorillonite.

The air-dry arable soil crumbs slaked upon wetting (Weston Turville less severely than Barnfield) while crumbs from the grassland soils remained intact after immersion in water.

Soil conditioner

VAMA, a co-polymer of vinyl acetate and a monoester of maleic acid, supplied by the Monsanto Chemical Company.

3. *Experimental*

(*a*) *Micro-structure of the soil crumbs*

Thin sections of the soil crumbs were made using Kubiëna's technique but impregnating with a cold-setting resin (Kubiëna, 1938; Osmond and Stephen, 1957).

Results

Apart from a few large pores due to root channels no marked difference could be seen between the sections from arable and grassland crumbs when viewed through a polarizing microscope (×70), both showing a brown-earth fabric (Kubiëna, 1954). The sections consisted of sand grains, often coated with orientated clay, together with small areas of orientated clay distributed at random in the general matrix. Orientated clay was not associated with iron concretions, calcite crystals, or root channels. Thus, the organic matter which strengthens the crumbs so as to inhibit their break-up on wetting did not appear to alter the arrangement of the primary particles in the crumbs.

(*b*) *The swelling of soil crumbs*

Soil crumbs were cut with a scalpel to make them as regular in shape as possible and then placed in specimen tanks in a desiccator containing

P_2O_5. When the crumbs were dry, lateral and vertical measurements of them were made with a travelling microscope fitted with a micrometer head reading to 0·002 cm. The dry crumbs were then transferred in the specimen tanks to a desiccator containing a water source and a slow capillary siphon. The desiccator was evacuated and the crumbs wetted slowly overnight to prevent slaking. Another series of soil crumbs was wetted in the same way with 0·01 M $CaCl_2$. Next day, lateral and vertical dimensions of the crumbs immersed in water and 0·01 M $CaCl_2$ were taken.

Results

The increase in lateral and vertical measurements in water and 0·01 M $CaCl_2$ is expressed as a percentage of the lateral and vertical measurements of the crumbs dried over P_2O_5 (Table 1).

TABLE 1

The Swelling of Soil Crumbs (per cent.)

	Distilled water		*0·01 M* $CaCl_2$	
	Lateral	*Vertical*	*Lateral*	*Vertical*
Highfield (grassland) . . .	8·9	9·0	9·0	9·2
Barnfield (arable) . . .	8·4	8·5	8·4	9·9
Weston Turville (grassland) . .	12·9	13·0	13·4	12·3
Weston Turville (arable) . .	14·8	14·4	12·8	14·5

These results show that within experimental error the swelling of the grassland and arable soil crumbs, of both Rothamsted and Weston Turville soils, is the same. It should be noted that there is no additional swelling in water compared with 0·01 M $CaCl_2$.

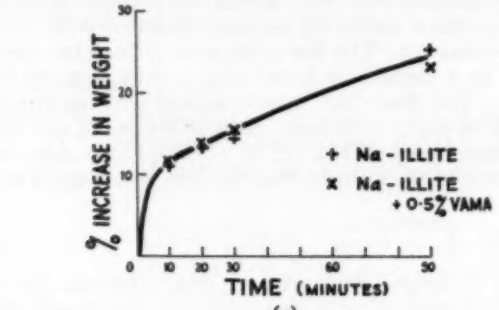
(*c*) *The rate of water uptake by clay flakes and soil crumbs*

(i) *Clays.* Na-illite and Na-illite+0·5 per cent. VAMA (by weight).

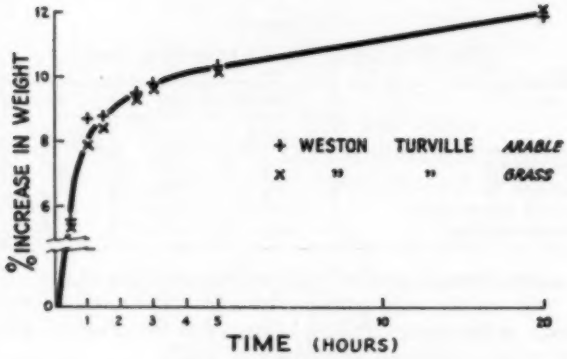
(ii) *Soils.* 1–2 mm. sieved crumbs from Weston Turville arable and grassland sites.

(iii) *Synthetic soil crumbs.* Highfield and Hoos ley soils were mixed with sufficient distilled water to make a sticky paste. The paste was forced through a 3-mm. sieve, and the resultant crumbs consisting of cylinders about 5 mm. long were dried over P_2O_5. Similar crumbs were made with Highfield and Hoos ley soil which had been pretreated with 40-volume H_2O_2 to destroy all the organic matter present.

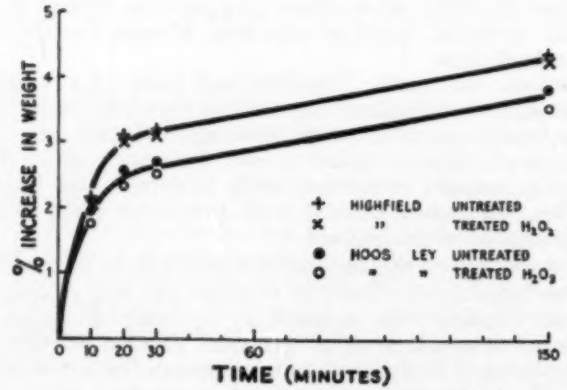
Rate of water uptake measurements were made on the clay flakes and soil crumbs listed above. Samples of about 150 mg. of clay, or about 1·5 g. of soil crumbs, were weighed dry in weighing bottles and then exposed to an atmosphere of 98 per cent. relative humidity above a saturated solution of barium nitrate in a vacuum desiccator at 15 mm. of mercury. The desiccator was immersed in a water bath maintained at 25±0·2° C. The desiccator was removed after 10 min. and the bottles weighed as rapidly as possible. It was then replaced and the procedure



(*a*)



(*b*)



(*c*)

FIG. 1. Rate of water uptake from an atmosphere at 98 per cent. relative humidity.

repeated after 20 and 30 min., and again after longer periods until the weight of the sample was approximately constant.

Results

It may be seen from Fig. 1*a* that the addition of VAMA to Na-illite has not altered its rate of uptake of water. Fig. 1*b* shows the percentage increase in weight of Weston Turville soil crumbs over their dry weight (over P_2O_5) graphed against time. There is no significant difference between the rate of water uptake by the permanent grassland or corresponding arable soil. The rate of water uptake by the synthetic soil crumbs is shown graphically in Fig. 1*c*. The soils in which the organic matter had been destroyed by H_2O_2 took up water at the same rate as the untreated soils.

In combination, these results show that organic matter does not depress the rate of water uptake by soil crumbs below a relative humidity of 98 per cent. (pF 4·45), so that the crystalline-water uptake by the clay is unaffected.

(*d*) *The effect of remoulding on the slaking of soil crumbs*

Arable and grassland remoulded crumbs were made by making a stiff paste from the crumbs and then squeezing the paste through a 3-mm. sieve to form cylinders about 5 mm. long. The slaking of these crumbs in distilled water was compared with that of natural 3–5 mm. sieved crumbs using a mechanically operated wet-sieving machine, working at 30 strokes per minute with a 1½ in. stroke length. This rate was chosen so that, provided the topmost sieve was always under water, the slaked fragments were separated without appreciable further mechanical breakdown. Twenty-five grammes of crumbs were used in each test. These were dried over P_2O_5 and then wetted by immersion to obtain severe and reproducible slaking conditions. None of the crumbs was treated with H_2O_2.

Results

Duplicate determinations agreed to within ±0·5 per cent. and the means are given in Table 2. In agreement with previous workers the wet strength of the natural grassland crumbs was found to be very much

TABLE 2

A Comparison of the Slaking of Natural and Remoulded Soil Crumbs

Sieve opening (mm.)	*Highfield (grass)* % *wt. retained on sieve*		*Barnfield (arable)* % *wt. retained on sieve*	
	Natural	*Remoulded*	*Natural*	*Remoulded*
4	3	0	0	0
2	88	0	0	0
1	3	1	1	1
0·5	1	2	2	1
0·25	1	16	7	6

higher than that of the arable crumbs. Most of the 3 per cent. of Barnfield soil retained on the coarse sieves was pure sand. The striking effect was the large reduction in the strength of the remoulded grassland crumbs, there being, for example, no water-stable crumbs larger than 2 mm. left after remoulding, compared with 88 per cent. from the natural crumbs. The reduction in strength of the much weaker Barnfield crumbs was very small. Beacher and Strickling (1955) found a general reduction in aggregate stability on remoulding crumbs.

(*e*) *The effect of remoulding on the dispersion of soil crumbs*

The dispersion of the crumbs was measured by end-over-end shaking of the crumbs in cylinders containing 1,000 c.c. of distilled water and rotated at 21½ r.p.m. Twenty-five grammes of crumbs dried over P_2O_5 were used for each test and the crumbs were wetted by immersion. The shaking was stopped periodically and three particle size fractions, $< 50\mu$, $< 20\mu$, and $< 2\mu$, were determined by sedimentation and a plummet balance (Marshall, 1956). After a total shaking period of 57 hours, 10 c.c. of 10 per cent. 'calgon' was added, and the particle size distribution again measured after a further 18½ hours' shaking. For comparison, mechanical analyses of the crumbs were made using the International method.

Results

In Figs. 2*a* and 2*b* the results marked 'calgon' are still on the time scale. The complete mechanical analysis on the extreme right-hand sides of the figures is given for comparison. The wet strength of the crumbs may be gauged from the amount of a given sized fraction in suspension as compared with the maximum possible amount indicated by the mechanical analysis. On this basis it may be seen that the wet strength of the grassland crumbs is much greater than that of the arable crumbs, as would be expected. The other main difference between the soils is that, whereas the breakdown of the arable crumbs was unaffected by remoulding, the percentage of particles smaller than 50μ or 20μ in the natural grassland crumbs only approached that of the remoulded grassland crumbs after 57 hours' shaking. The aggregation of the clay fraction was unaffected by remoulding. Even for the arable crumbs, this fraction was only partially dispersed after 57 hours' shaking. This implies a considerable aggregation of the clay, as from long-term settling of the completely dispersed suspension the equivalent spherical diameter of some of the smallest particles is less than $0{\cdot}1\mu$.

The amount of calgon added contained 12 m.e. Na^+ as compared with the cation exchange capacity of 25 g. of soil of 4 m.e. This would be sufficient to convert the initially calcium-saturated soil into a sodium soil. Barnfield soil was completely dispersed by this treatment, including, in particular, the clay fraction. The aggregation of the 50μ and 20μ fraction of the grassland soil was reduced but not destroyed by this treatment, and the aggregation of the clay fraction was unaffected. The latter is in accord with previous measurements of the resistance to dispersion of the clay in grassland crumbs, when it was found that this was

not reduced by leaching with a solution of neutral sodium pyrophosphate (Emerson, 1956).

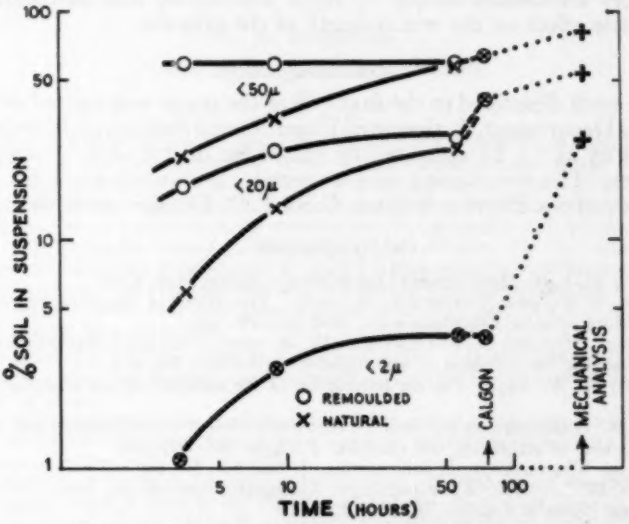


FIG. 2*a*. Dispersion of Highfield Grassland crumbs.

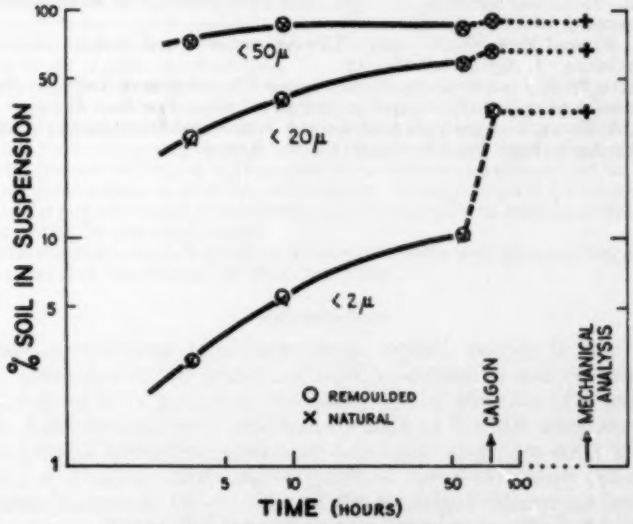


FIG. 2*b*. Dispersion of Barnfield Arable crumbs.

The slaking and dispersion tests together show that the particular method of remoulding used does not affect the aggregation of the clay

fraction, but can disrupt many of the bonds holding 50 μ and 20 μ sized particles together. In the arable crumbs most of these bonds are so weak that they are broken simply by rapid wetting, so that remoulding had very little effect on the wet strength of the crumbs.

Acknowledgements

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REFERENCES

BAVER, L. D. 1956. Soil Physics (3rd edition). Wiley, New York.

BEACHER, B. F., and STRICKLING, E. 1955. The effect of puddling on the water stability of some Maryland soils. Soil Sci. **80**, 363.

DETTMANN, Margaret G., and EMERSON, W. W. 1959. A modified permeability test for measuring the cohesion of soil crumbs. J. Soil Sci. **10**, 215.

EMERSON, W. W. 1954. The determination of the stability of soil crumbs. Ibid. **5**, 233.

—— 1956. A comparison between the mode of action of organic matter and synthetic polymers in stabilizing soil crumbs. J. Agric. Sci. **47**, 350.

—— 1959. The structure of soil crumbs. J. Soil Sci. **10**, 235.

KUBIËNA, W. L. 1938. Micropedology. Collegiate Press, Ames, Iowa.

—— 1954. Soils of Europe. Murby, London.

MARSHALL, T. J. 1956. A plummet balance for measuring the size distribution of soil particles. Australian J. Appl. Sci. **7**, 142.

OSMOND, D. A., and STEPHEN, I. 1957. The micropedology of some red soils from Cyprus. J. Soil Sci. **8**, 19.

PURI, A. N., and KEEN, B. A. 1925. The dispersion of soil in water under various conditions. J. Agric. Sci. **15**, 147.

SCHOFIELD, R. K., and SAMSON, H. R. 1954. Flocculation of kaolinite due to the attraction of oppositely charged crystal faces. Disc. Far. Soc. **18**, 135.

TIULIN, A. F. 1928. Aggregate analyses as a method for determining soil structure. Perm Agric. Exp. Sta. Div. Agric. Chem., Rep. **2**, 77.

THE STRUCTURE OF SOIL CRUMBS

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Summary

A model of a soil crumb is proposed in which the crumb consists of domains of orientated clay and quartz particles. A clay domain is defined as a group of clay crystals which are orientated and sufficiently close together to behave in water as a single unit. In normal agricultural soils, where calcium is the dominant exchangeable cation, the clay crystals in the crumbs are all aggregated into domains by drying. Drying to the wilting point is apparently sufficient. In the model the domains and the quartz particles may be linked to each other by organic matter or soil conditioners. The domains may also be held together by electrostatic forces.

The model satisfies four conditions derived from experiment on the effect of organic matter on soil crumbs:

1. The crystalline swelling of the clay in the crumb is unaltered—the individual crystals within the domains are unaffected by organic matter and are free to take up water.
2. Slaking is prevented—the strains set up in the crumb on wetting are shared between several domains through their common linkages by organic matter to quartz particles.
3. Dispersion of Na-saturated crumbs is prevented—the linkages of the domains by organic matter restrain the diffuse double layer swelling of the clay.
4. pF—moisture content curve is unaltered—the stabilization by organic matter does not require a rearrangement of the structure of the crumb.

On the basis of the model, conventional wet-sieving or dispersion tests assess the strength of the organic-matter linkages. Remoulding crumbs breaks many of the previously stable quartz-domain bonds, so that on drying and re-testing the stability of the crumbs has decreased.

The model has been shown to be consistent with present knowledge of the action of cement and lime in stabilizing soil, cement or lime being substituted for organic matter in the model. It also accounts qualitatively for the sensitivity of soils, that is the decrease in shear strength after remoulding. On the basis of the model the amount of organic matter resistant to microbial attack should be proportional to the surface area of the clay domains. Remoulding soil (or tillage) by breaking the organic-matter bonds joining the clay domains to the quartz will free organic matter for microbial attack.

This model does not apply to soil crumbs in which the crystalline swelling of the clay is prevented, for example by heat treatment.

1. *Introduction*

In earlier experiments (Emerson 1954, 1956*a*, 1956*b*) it was found that the resistance to dispersion of sodium-saturated soil crumbs was much increased by a period under grass, or the addition of a soil conditioner. Carboxylated soil conditioners such as VAMA were shown to form peripheral complexes, whereas non-ionic polymers such as PVA (polyvinyl alcohol) formed inter-crystalline complexes with Na-montmorillonite (Emerson, 1955). One of the principal differences between these two types of complex formation was found to be the behaviour of the complexes after leaching with a 0·1 M neutral sodium pyrophosphate solution. On immersing the complexes in N NaCl and then reducing the salt concentration, the peripheral complexes dispersed at the same con-

centration of NaCl as the untreated clay whereas the wet strength of the inter-crystalline complexes was unaffected. As grassland crumbs were still stable in water after this treatment, it was inferred that the clay in the crumbs was stabilized by the formation of inter-crystalline complexes (Emerson, 1956*b*). If this were so, then water uptake by the clay should be reduced, since the basal surfaces of the clay crystals covered by the organic matter would be unable to take up their crystalline water layers. This reduction in crystalline water uptake would cause a corresponding decrease in the swelling of the clay and hence a reduction in the swelling of the soil crumbs. As reported in the preceding paper, however (Emerson and Dettmann, 1959), the crystalline swelling and water uptake of arable and grassland crumbs were found to be the same experimentally. The hypothesis of organic matter forming inter-crystalline complexes was therefore untenable.

2. *The Constituents of Soil Crumbs*

The two main constituents of soil are quartz and clay. The surface soil crumbs are continually being broken down into these constituents by mechanical action, principally that of raindrops. In normal soils there is insufficient salt present to reflocculate the clay completely, so that crumbs are subsequently reformed from quartz and dispersed clay. In the absence of salts flocculation may occur by positive edge–negative face attraction between the individual clay crystals, but this type of flocculation may be excluded in general for two reasons. Firstly, because conditions are unfavourable if the clay is Ca-saturated; secondly, even with kaolinite crystals, the arrangement is inhibited by the presence of a small admixture of montmorillonite or illite (Schofield and Samson, 1954).

Evidence from the electron microscope (Shaw, 1942; Bates, 1958), microscope (Emerson, 1956*c*), and from the (001) X-ray reflections in powder specimens (Norrish, 1954), shows that montmorillonite crystals dried from dispersed suspensions are ordered in the (001) plane. Electron micrographs (Bates, 1958) also indicate that kaolinite and illite crystals behave similarly. Hence, the clay crystals in soil crumbs formed by drying will be orientated. Such areas of orientated clay were observed by Brewer and Haldane (1957) in thin sections of synthetic quartz-clay mixtures.

After air-drying, flakes of orientated calcium-saturated clay do not disperse in distilled water, unless mechanically disturbed (Emerson, 1954). This is due to an energy barrier at a critical distance of separation of the clay crystals, the distance being 10 Å. for Ca-montmorillonite (Norrish, 1954). In this paper a clay domain is defined as a group of clay crystals having suitable exchangeable cations which are orientated and sufficiently close together for the group to behave in water as a single unit. In a domain of illite, for example, each crystal consists of several structural silica-aluminium sheets tightly bound together, so that water cannot enter between the sheets. However, water is taken up between each crystal and the domain swells as a whole. The precise restrictions on the composition of the exchangeable cations so that there is an energy barrier preventing the dispersion of the orientated clay in water are not

yet known. Clearly in the extreme case of all the cations being sodium ions no domains are formed.

Starting with a suspension of dispersed calcium clay it is of interest to know how much drying is necessary before all the clay crystals are brought sufficiently close together to be aggregated into domains. For Ca-montmorillonite, this appears to occur at about pF 4·2 (Warkentin *et al.*, 1957) and for London Clay at pF 4·5 (Croney and Coleman, 1954). It seems likely that drying by plant roots alone would be sufficient for this.

For soil crumbs containing a mixture of 1:1 and 2:1 layer silicate minerals, e.g. kaolinite and illite (the most usual case in soils), it is possible that the clay crystals would segregate into domains of pure illite or kaolinite. The basal surface of the smaller illite domains could be held against the edges of the kaolinite domains by electrostatic attraction, in a similar way to individual kaolinite and illite crystals (Schofield and Samson, 1954).

The second main constituent of soil crumbs, quartz, occurs over a wide range of particle sizes from coarse sand to $< 2\,\mu$ diameter particles.

3. *The Interaction of Soil Crumbs and Polymers*

It is now proposed that soil organic matter and soil conditioners stabilize soil crumbs by increasing the strength of the quartz-clay bonds in the crumbs as shown diagrammatically in Fig. 1 (Emerson, 1959). For this to be possible, the carboxylated polymers and PVA, in addition to bonding clay crystals together, must also be able to form bonds with quartz surfaces. VAMA has been found to form water-stable aggregates from pure quartz particles by Burnett (1953) and by Hagin and Bodman (1954). In laboratory experiments, adding 0·5 per cent. by weight of VAMA or PVA to the fine sand fraction of Barnfield soil gave aggregates which were not broken up by shaking in water. In Fig. 1 PVA and soil organic matter are shown as forming a complex between the quartz and the basal surface of the clay domain. The scale of the polymers is grossly exaggerated with respect to that of the quartz particles. The dimensions of a single molecule of a typical carboxylated soil conditioner (VAMA) are about 60 Å. × 3 Å., and as the average diameter of a clay crystal is 500 Å., several polymer chains could be absorbed at each quartz-clay boundary.

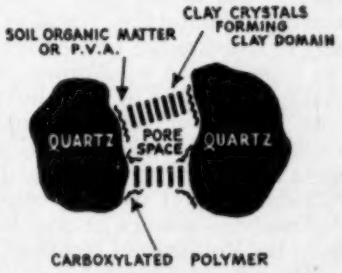

FIG. 1. A simplified model of a soil crumb.

The proposed model of soil-polymer interaction satisfies two necessary conditions:

1. The crystalline water uptake by the clay in the soil crumbs and the swelling of the crumbs are unchanged by the presence of the polymer (Emerson and Dettmann, 1959).

2. No alteration in the spatial distribution of the crumb constituents is required to accommodate the polymer. This condition is necessary because the structure of arable and grassland crumbs as shown in thin sections is similar (Emerson and Dettmann, 1959). This implies that the pore size distribution (apart from large root channels) is also unchanged by the presence of the polymer. Similar pF-moisture content curves have been found for grassland and cultivated soils (Jamison and Kroth, 1958) and for VAMA treated and untreated soils (Peters, Hagin, and Bodman, 1953; Wittmuss and Mazurak, 1958).

In addition, the model must account for the resistance of the crumbs to slaking, and of the clay to dispersion even after Na-saturation.

The stresses set up in a dry soil crumb due to wetting are large. Ca-montmorillonite, for example, completes its crystalline water uptake at 96 per cent. relative humidity (Grudemo, 1956). Hence, if dry Ca-montmorillonite were placed on a membrane in contact with free water a pressure of at least 50 atmospheres would have to be applied to prevent this degree of swelling. For a crumb to be stable to rapid wetting, there must be some means of equalizing the stresses at the wetting front induced by the swelling of the clay domains. In the present model, this is provided by the linkage of several clay domains to each quartz particle.

Secondly, laboratory experiments have shown that the linear dimensions of Na-saturated Highfield crumbs (permanent grass) increased by only 4 per cent. on reducing the NaCl concentration from N to N/20, whereas the corresponding increase for the Barnfield crumbs (permanent arable) was 22 per cent. The quartz-clay linkages, whilst not strong enough to inhibit the crystalline swelling, prevent dispersions of the Na-clay by reducing the diffuse double-layer swelling of the clay as the crumbs are brought into equilibrium with successively lower concentration of NaCl. The effect of these linkages on swelling would not be detected with the natural calcium-saturated crumbs, as there is no double-layer swelling in this case, the swelling of the crumbs being found to be the same in both M/100 $CaCl_2$ and water (Emerson and Dettmann, 1959). Schofield (1935) using freezing-point depression measurements also deduced the absence of double-layer swelling in Ca-saturated crumbs from the Rothamsted Hoosfield.

The scheme proposed is in accordance with the results of Hagin and Bodman (1954) who found that the aggregation of quartz-kaolinite and quartz-montmorillonite mixtures by VAMA depended only on the external surface area of the clay (as measured by nitrogen absorption), which for these synthetic mixtures is a good first approximation to the surface area of the clay domains. They also found that 0·1 per cent. by weight of VAMA added to a pure quartz sand by itself resulted in 40 per cent. of water-stable aggregates, whereas the same amount of conditioner with 2·5 per cent. of montmorillonite gave 100 per cent. of water-stable aggregates. Stabilizing sand only with a soil conditioner must be an inefficient process, since if a polymer molecule becomes attached to one particle it has little chance of linking to another particle, as the area of contact of the sand grains is small compared with the total surface area of the particles.

The model also elucidates the mechanics of soil conditioner-crumb interaction. As a solution of a soil conditioner penetrates into dry soil, the swelling of the clay domains breaks the weakest quartz-clay bonds and separates the clay domains in the soil crumbs. This process produces readily available sites for the absorption of the polymer which are, at the same time, the most advantageous for improving crumb stability. If crumbs treated in this way with soil conditioner are then remoulded, the remoulding will break further quartz-clay bonds which were strong enough originally to withstand the sudden wetting of the crumbs (by the solution of conditioner) either due to a favourable spatial situation or organic matter bonding. Hence after drying and re-testing the crumbs will again slake appreciably. This has been demonstrated by Laws (1954) and Grossi and Woolsey (1955). As a corollary, the amount of a soil conditioner required to stabilize a soil is greater for remoulded than for undisturbed crumbs (Hénin *et al.*, 1956).

The ease with which many of the quartz-clay bonds in grassland crumbs are broken by remoulding implies that the organic matter is held to the quartz by weak secondary valence forces (hydrogen bonds). This would be expected on chemical grounds as a quartz surface consists of tetrahedrally linked silicon atoms. However, in some soils, quartz is coated with sesquioxides which could increase the strength of the quartz-clay bonds.

4. *A Generalized Model of a Soil Crumb*

Fig. 1, in which the quartz particles were shown linked by single domains whilst containing the essential components, is over-simplified, the possible arrangements in a soil crumb being far more complicated (see Fig. 2). The quartz particles may be linked directly by organic matter (A) or through two or more domains, which are themselves linked by organic matter (C_1). Some clay domains may be held together by electrostatic attraction between the positive edges and negative faces (D). It is also probable that a proportion of the organic matter is linked in the same manner as proposed for carboxylated polymers, as in a previous paper (Emerson and Dettmann, 1959), adding 'calgon' did slightly increase the dispersion of the grassland crumbs. Hence linkages like C_1 and C_2 are possible. The domains themselves vary in the size and number of individual crystals of which they are composed.

5. *The Measurement of the Stability of Soil Crumbs*

On the basis of the model, the stability of a soil as assessed by any conventional slaking technique, such as wet sieving, is a measure of the number of quartz-domains bonds broken by the rapid swelling of the domains on wetting. The particular results obtained depend on the speed and amount of swelling of the domains, i.e. initial moisture content of the crumbs (Panabokke and Quirk, 1957) and rate of wetting of the crumbs (Emerson and Grundy, 1954).

The sodium-saturation test was developed to distinguish between factors influencing the breakdown of dry crumbs on wetting (slaking)

and those affecting the wet strength of the crumbs. If the effect of organic matter on crumb cohesion is being investigated, then the sodium-saturation test gives similar results to any conventional slaking test (Dettmann and Emerson, 1959), as the same organic matter bonds prevent both slaking of the dry crumbs and dispersion of the wet Na-crumbs.

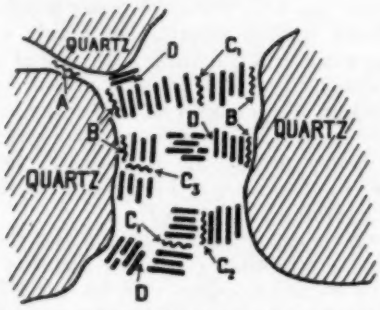

FIG. 2. Possible arrangements of domains, organic matter, and quartz in a soil crumb.

Type of Bond: A. Quartz—Organic Matter—Quartz
B. Quartz—Organic Matter—Domain
C. Domain—Organic Matter—Domain { C_1, face—face; C_2, edge—face; C_3, edge—edge }
D. Domain—Domain, edge—face

However, there are conditions, such as the presence of trivalent cations on the exchange complex, which do not affect the crystalline swelling of the clay, and therefore slaking, but do increase the wet strength of the crumbs (Emerson and Dettmann, unpublished).

Apart from linkage by organic matter the quartz-domain bonds themselves have a certain intrinsic strength. In the original sodium-saturation test (Emerson, 1954) in which a bed of crumbs was percolated with successively lower concentrations of NaCl, it was found that crumbs from Barnfield 80 and Willalooka sub-soil (for detailed descriptions of the soils see Emerson and Dettmann, 1959) collapsed, with dispersed clay appearing in the leachate, at the same NaCl concentration as was required to flocculate the separated Na-clay. This indicates that the restraining effect of the quartz-clay bonds on the double-layer swelling of the clay domains was very small, i.e. the quartz-clay bonds were very weak in these soils.

The above model of a soil crumb applies only to soil crumbs in which the clay domains are free to take up their inter-crystalline water. There are several methods of stabilizing soil crumbs by inhibiting the inter-crystalline swelling of the clay, e.g. heating (Dettmann, 1958) or using quaternary ammonium salts (Grossi and Woolsey, 1955).

The model does not apply to crumbs in which the clay is pure kaolinite (see section 2). Laboratory experiments have shown (Emerson, unpublished) that orientated flakes of kaolinite swell normally (i.e. in the

same manner as illite and montmorillonite) at low moisture contents, but on immersion in water a rearrangement of the kaolinite crystals occurs causing instability and collapse. Bodman and Hagin (1954) found that no water-stable aggregates were produced by adding up to 20 per cent. by weight of kaolinite to quartz particles.

6. *Some Applications of the Proposed Model*

(*a*) *Stabilization of soil with cement and hydrated lime*

Portland cement has been used extensively to stabilize soil for roads and runways. Marshall (1954) has compared the water absorption of soil-cement mixtures, soil and pre-hydrated cement. From the values obtained for soil alone and for pre-hydrated cement alone, the amount absorbed by an inert mixture of these two was calculated. His results at 50 per cent. relative humidity are given in Table 1 together with the clay content of the soils ($< 2\ \mu$).

TABLE 1

Water Absorbed at 50 per cent. Relative Humidity by Soil Cement and by an Equivalent Mixture of Soil and Pre-hydrated Cement (12 per cent. by weight)

Soil	*Clay %*	*Water content %*		
		Soil only	*Soil-cement*	*Soil and pre-hydrated cement calculated*
Roto . . .	19	2·6	2·8	2·8
Adelaide . .	17	1·3	2·2	1·7
Mallala . .	46	6·6	5·7	6·4
Gawler . .	20	2·1	2·4	2·5
Sprent . .	60	6·0	5·2	5·8

Water uptake at 50 per cent. relative humidity water absorption is due to the crystalline swelling of the clay and not to pore filling. Hence from Table 1 it may be inferred that the cement does not penetrate between the internal surfaces of the clay domains. It is suggested that cement, as well as linking quartz particles together, also links the external surfaces of the clay domains to the quartz in the same manner as soil organic matter or a soil conditioner.

Little is known of the mechanism by which soil may be slowly stabilized by the addition of hydrated lime. Clare and Cruchley (1957) added 4 per cent. lime to six clay soils, and found no reduction in the amount of water held at pF 2·4 even after twelve months, although the treatment did result in a progressive increase in the plastic limit of the soils. Also Goldberg and Klein (1952) showed by X-ray examination that the uptake of the first water layer by montmorillonite was unaffected by adding 8 per cent. by weight $Ca(OH)_2$ to montmorillonite and then leaving the clay to air-dry slowly for a fortnight. The only available evidence is thus consistent with the lime reacting with the external surface of the clay domains in a similar physical way to cement.

(*b*) *The sensitivity of soils*

This is defined by workers in soil mechanics as the ratio of the shear strength of undisturbed soil to that of remoulded soil. The shear strength depends on the cohesion of the clay domains and on the strength of the quartz-clay bonds. According to results given by Emerson and Dettmann (1959), para. 3 (*d*), remoulding a calcium soil does not alter the aggregation of the clay. For normal over-consolidated soils (low-strength quartz-clay bonds) the remoulded shear strength is somewhat reduced (Skempton and Northey, 1952) according to the number of quartz-clay bonds broken. By contrast, the clay domains in a sodic soil would be expected to be susceptible to deformation by remoulding. The lower the concentration of electrolyte in the sodic soil, the lower the resistance of the clay domains to deformation, and hence the greater the reduction in remoulded shear strength and the higher the sensitivity (Skempton and Northey, 1952; Newland and Allely, 1956). The decrease in shear strength will be particularly marked in a sodium soil containing organic matter (Soderblom, 1958), the remoulding not only breaking the linkages between quartz, organic matter, and clay but also permitting dispersion of the clay. To make the theory quantitative further dispersion tests need to be made on untreated and remoulded soils together with shear strength measurements.

(*c*) *The resistance to breakdown of bonded organic matter in soil crumbs*

Rovira and Greacen (1957) found an increase in microbial activity after shearing wet soil crumbs. These authors ascribed their results to organic matter becoming available which was previously shielded from microbial attack by being held in pores too small for micro-organisms to enter. Shearing, like remoulding, will break many of the quartz-clay bonds so that organic matter could also be freed for microbial attack which before was joined chemically to both clay and quartz. Other workers have shown that the protective action of montmorillonite on the breakdown of proteins by enzymes (Ensminger and Gieseking, 1942; Pinck, Dyal, and Allison, 1954) is restricted to a monolayer on the surface of the montmorillonite. On the present model of a soil crumb the maximum amount of totally protected organic matter corresponds to a monolayer over the interfaces between domains and quartz, that is, approximately over the external surface area of the clay domains. Hedrick and Mowry (1952) perfused a bed of soil crumbs treated with 0·1 per cent. by weight VAMA for three years without any evidence of microbial breakdown. Martin (1953) found a similar result over a shorter period of time using crumbs to which 0·05 per cent. by weight of another carboxylate polymer had been added. It should be noted that in a pure sand the protected organic matter would be confined to the parts of contact of the sand grains.

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REFERENCES

BATES, T. F. 1958. Electron micrographs of clays. Penn. State Coll. Circ. 51.

BREWER, R., and HALDANE, A. D. 1957. Preliminary experiments in the development of clay orientation in soil. Soil Sci. **84**, 301.

BURNETT, E. 1952. The effect of synthetic polyelectrolytes on certain physical properties of several soils. Ph.D. Thesis, Ohio State University. (Quoted by MARTIN, W. P., 1953, Soil Sci. Soc. Amer. Proc. **17**, 1.)

CLARE, K. E., and CRUCHLEY, A. E. 1957. Stabilization of clays with hydrated lime. Geotechnique, **7**, 97.

CRONEY, D., and COLEMAN, J. D. 1954. Soil structure in relation to soil suction. J. Soil Sci. **5**, 75.

DETTMANN, M. G. 1958. Water uptake by pure clays and soil crumbs. Ibid. **9**, 306.

—— and EMERSON, W. W. 1959. A modified permeability test for measuring the cohesion of soil crumbs. Ibid. **10**, 215.

EMERSON, W. W. 1954. The determination of the stability of soil crumbs. Ibid. **5**, 233.

—— 1955. The interaction of montmorillonite with high polymers. Nature, **176**, 461.

—— 1956*a*. Synthetic soil conditioners. J. Agric. Sci. **47**, 117.

—— 1956*b*. A comparison between the mode of action of organic matter and synthetic polymers in stabilizing soil crumbs. Ibid. **47**, 350.

—— 1956*c*. Liquid crystals of montmorillonite. Nature, **178**, 1248.

—— 1959. The stability of soil crumbs. Ibid. **183**, 538.

—— and DETTMANN, M. G. 1959. The effect of organic matter on crumb structure. J. Soil Sci. **10**, 227.

—— and GRUNDY, G. M. F. 1954. The effect of rate of wetting on water uptake and cohesion of soil crumbs. J. Agric. Sci. **44**, 249.

ENSMINGER, L. E., and GIESEKING, J. E. 1942. Resistance of clay absorbed proteins to proteolytic hydrolysis. Soil Sci. **53**, 209.

GOLDBERG, I., and KLEIN, A. 1952. Some effects of treating expansive clays with calcium hydroxide. A.S.T.M. Spec. Pub. **142**, 53.

GROSSI, F. X., and WOOLSEY, J. L. 1955. Effect of fatty quaternary ammonium salts on some physical properties of Ohio soils. Ind. Chem. Engng. **47**, 2253.

GRUDEMO, A. 1956. Research in Progress No. 5. Swedish Cement and Concrete Res. Inst., Roy. Inst. Tech. Stockholm.

HAGIN, J., and BODMAN, G. B. 1954. Influence of the polyelectrolyte CRD–186 on physical properties of soils and clay minerals. Soil Sci. **78**, 367.

HÉNIN, S., CARDEY, F., and ROESCH, A. 1956. Mode d'action des conditionneurs de sol. Rapp. VI Int. Congr. Soil Sci. **13**, 53.

JAMISON, V. C., and KROTH, E. M. 1958. Available moisture storage capacity in relation to textural composition and organic matter content of several Missouri soils. Soil Sci. Soc. Amer. Proc. **22**, 189.

LAWS, W. D. 1954. The influence of soil properties in the effectiveness of synthetic soil conditioners. Ibid. **18**, 379.

MARSHALL, T. J. 1954. Some properties of soil treated with Portland cement. Symposium on Soil Stabilization. Commonw. Australia, Dept. Supply, p. 28.

NEWLAND, P. L., and ALLELY, B. H. 1956. Results of some investigations on two sensitive clays. Proc. 2nd Aust.-N.Z. Conf. Soil Mech.

NORRISH, K. 1954. The swelling of montmorillonite. Disc. Faraday Soc. **18**, 120.

PANABOKKE, C. R., and QUIRK, J. P. 1957. Effect of initial water content on the stability of soil aggregation in water. Soil Sci. **83**, 185.

PETERS, D. B., HAGAN, R. M., and BODMAN, G. B. 1953. Available moisture capacities of soils as affected by additions of polyelectrolyte soil conditioners. Ibid. **75**, 467.

PINCK, L. A., DYAL, R. S., and ALLISON, F. E. 1954. Protein montmorillonite complexes, their preparation and the effects of soil micro-organisms on their decomposition. Ibid. **78**, 109.

POTTER, R. S., and SNYDER, R. S. 1956. Carbon and nitrogen charges in soils variously treated. Ibid. **1**, 76.

ROVIRA, A. D., and GREACEN, E. L. 1957. The effect of aggregate disruption on the activity of micro-organisms in the soil. Aust. J. Agric. Res. **8**, 659.

SCHOFIELD, R. K. 1935. The interpenetration of the diffuse double layers surrounding soil particles. Trans. Third Int. Cong. Soil Sci. **1**, 30.

—— and SAMSON, H. R. 1954. Flocculation of kaolinite due to the attraction of oppositely charged crystal faces. Disc. Faraday Soc. **18**, 135.

SHAW, B. D. 1942. The nature of colloidal clay as revealed by the electron microscope. J. Phys. Chem. **46**, 1032.

SKEMPTON, A. W., and NORTHEY, R. D. 1952. The sensitivity of clays. Geotechnique, **3**, 30.

SODERBLOM, R. 1957. Some investigations concerning salt in clay, IV. Int. Congr. Soil Mech. **1**, 111.

WARKENTIN, B. P., BOLT, G. H., and MILLER, R. D. 1957. Swelling pressure of montmorillonite. Proc. Soil Sci. Soc. Amer. **21**, 495.

WITTMUSS, H. D., and MAZURAK, A. P. 1958. Physical and chemical properties of soil aggregates in a brunizem soil. Ibid. **22**, 1.

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STUDIES ON THE ORGANIC MATERIAL EXTRACTED FROM SOILS AND COMPOSTS

I. THE ISOLATION AND CHARACTERIZATION OF LIGNO-PROTEINS FROM COMPOST

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Summary

A modification of the Sevag technique for removing proteins from aqueous solution was applied to sodium-pyrophosphate and sodium-sulphite extracts of the water-insoluble part of a wheat-straw compost. Fifty-seven per cent. of the nitrogen in the sulphite extract and 42 per cent. of that in the pyrophosphate extract was removed by this technique. This material was isolated and found to give 55–60 per cent. of its nitrogen as α-amino-acid nitrogen on acid hydrolysis. The non-hydrolysable part was very similar to lignin from wheat straw and is almost certainly derived from it with comparatively little modification. It follows that the term ligno-protein or perhaps 'ligno-peptide' provides a reasonable description of the material isolated.

The lignin in the 'ligno-protein' was sulphonated to a slight extent by sodium sulphite during the extraction.

IT has been known for many years that lignin is, of all the major plant constituents, by far the most resistant to decay. This stability led to the view that a considerable portion of the organic matter in soil is derived more or less directly from the lignin of plants. The ability of lignin to combine with proteins giving ligno-proteins with many of the properties of 'humic acids' isolated from soil gave rise to the theory (Waksman, 1938) that such complexes make up the major part of soil organic matter, in particular that fraction soluble in alkali and precipitable by acid.

The Sevag (1938) technique for removing proteins from aqueous solution has been applied by Tinsley and Zin (1954) to extracts of the organic matter of soils and composts. In this method the protein is adsorbed on the oil : water interface of the droplets which are formed when the aqueous solution is emulsified with chloroform or, better, carbon tetrachloride (Coulson, 1953). The droplets are thereby stabilized and can then be centrifuged down, carrying the protein with them. This technique is not specific for proteins: any colloidal material having both hydrophobic and hydrophillic areas on its surface will be adsorbed on the interface. Both lignin and ligno-protein come into this category as do some of the high molecular-weight condensed tannins. Zin (1955) found that only a small portion (4–10 per cent.) of the organic material extracted from a range of mineral soils by aqueous solutions of sodium sulphite and pyrophosphate could be removed by the Sevag technique,

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but that somewhat larger quantities could be isolated from similar extracts of compost. Upwards of 70 per cent. of the nitrogen in the interface-adsorbed material from both soils and compost could be obtained as α-amino-acid nitrogen on hydrolysis. The methoxyl content of the materials from mineral soils was uniformly lower than that of materials isolated from a compost.

The aim of the work described in this paper was to isolate gram quantities of the interface-adsorbed material from extracts of a compost of known history, to examine its properties, and to establish the presence or absence of lignin, with a view to comparing it with materials isolated by the same technique from mineral soils. A subsidiary aim was to compare the material extracted by sodium pyrophosphate under mild conditions with that extracted by hot sodium sulphite, a more efficient but more drastic reagent.

In the experimental section of this paper the interface-adsorbed material is arbitrarily called 'the ligno-protein fraction'; a justification of the use of this term will be found in the discussion. L.P.S. and L.P.P. refer to the ligno-proteins isolated from the sulphite and pyrophosphate extracts respectively.

Experimental Part

Analytical methods

Nitrogen was determined by the semi-micro Kjeldahl technique using the Hoskins distillation apparatus.

Methoxyl was determined by a modified Zeisel method (Zin, 1955). This reference also contains a detailed account of the Kjeldahl technique used throughout the present work.

Dry-matter determinations were carried out by drying for 24 hours in an oven with free air circulation at 80° C.

Microchemical analyses for carbon, hydrogen, and sulphur were carried out by Drs. Weiler and Strauss, Oxford.

Silica in ash was estimated by the procedure described by Vogel (1951).

Section 1

Isolation of Ligno-protein from Compost

Description of compost

The compost used is fully described by Tinsley and Nowakowski (1958). Table 1 gives the composition of the wheat straw used.

The compost was prepared from 25 kg. of this straw, 1·62 kg. of ammonium sulphate, 1·62 kg. of calcium carbonate, and sufficient water to bring the moisture content to 65 per cent. of the total wet weight. The initial carbon:nitrogen ratio was approximately 20. The results in Table 2 (partly taken from Tinsley and Nowakowski) show the changes taking place as rotting progressed.

If the methoxyl content of the compost be taken as a measure of the lignin content then the lignin decomposed initially at a slightly lower rate than the organic matter as a whole. However, in the later stages the

relative rate of lignin decomposition increased and at 480 days half of the original methoxyl and about half of the original organic matter had gone. Methoxyl content must be used with caution as a guide to lignin content in complex materials like soil and compost: at least two groups of compounds contribute, the lignins and the methylated carbohydrates. In addition Rudloff (1957) has shown that if glycerol, ethylene glycol,

TABLE 1

Composition of Wheat Straw

% *dry matter*	% *Ash**	% *total* N†	% *Methoxyl*†	% *Lignin*†‡
85·0	5·8	0·59	3·58	15·4

* Expressed as per cent. oven-dry material.
† Expressed as per cent. ash-free oven-dry material.
‡ Moon and Abou Raya's method (1954).

TABLE 2

Composition of Compost as Rotting Progressed

Time in days	% *Ash**	% *Original organic matter remaining*†	% *Original methoxyl remaining*	% *Original* N *remaining*
0	11·8	100	100	100
28	13·9	89	90	106
56	17·5	68	74	104
112	19·5	59	66	96
340	20·6	56	63	86
480	21·6	52	50	78

* Expressed as per cent. oven-dry material.
† Assuming that all of the ash originally present remains throughout.

sorbitol, or mannitol is present, high results will be obtained from the Zeisel determination. It is possible that small amounts of these and similar compounds are present in soils and composts, and that they are released by hydrolysis under the conditions of the methoxyl determination. However, even with these reservations it can be said that, after the first flush of decomposition, there is no evidence for the accumulation of a relatively unchanged lignin-rich fraction, the percentage of methoxyl being about the same after 480 days as at the beginning.

Extraction of water-soluble nitrogen from compost

After 480 days' decomposition, 4 kg. of the wet compost were removed for the work described below. A sample of this was air-dried directly. The remainder was made into a slurry with 12 litres of distilled water, filtered and washed twice more in the same way. The concentration of nitrate nitrogen and non-nitrate nitrogen in the washings was determined by the method of Tinsley and Nowakowski (1958). One-third of the washed compost was used directly without drying for the cold-pyrophosphate extraction as described later; the remainder was air

dried and ground to pass a 2-mm. sieve. Table 3 gives the composition of the compost before and after washing.

Extraction of water-insoluble nitrogen from compost

Two of the extractants recently introduced for the extraction of organic nitrogen from soils were used: sodium pyrophosphate (Bremner *et al.*, 1946) and sodium sulphite (Tinsley and Zin, 1954).

TABLE 3

Composition of Unwashed and Washed Compost

	% *Ash*•	% *Methoxyl*†	% N†	% *Nitrate nitrogen*† *removed by washing*	% *Non-nitrate nitrogen*† *removed by washing*
Unwashed compost	21·6	3·42	3·48	0·82	0·28
Washed compost	20·8	3·51	2·60	—	—

• Expressed as per cent. oven-dry material.
† Expressed as per cent. ash-free, oven-dry material.

Exploratory experiments had shown that only 20·8 per cent. of the compost nitrogen was dissolved from the dried washed compost by boiling for 1 hour with a 0·5 N sodium-pyrophosphate solution, whereas about twice this amount of nitrogen could be extracted by 0·5 N sodium sulphite under similar conditions. It was found, however, that larger amounts of nitrogen could be extracted by pyrophosphate if the compost had not been dried before extraction, and that, contrary to the case with sulphite, boiling did not greatly increase the amount of nitrogen brought into solution.

The sulphite extraction was carried out under the standard conditions of Tinsley and Zin, but on a larger scale. The dried washed compost (200 g. containing 185·8 g. oven-dry material) was refluxed with 2 litres of 0·5 N sodium sulphite for 1 hour, with vigorous stirring.

For the pyrophosphate extraction 1 kg. of the washed undried compost (containing 332 g. oven-dry material) was extracted with the required amount of water and sodium pyrophosphate to give a 0·5 N solution and an extractant:compost ratio of 13. This ratio was chosen because the extractant:compost ratio of 10 used in the sulphite extraction, and in previous work by Zin (1955), gave a slurry which was too thick to stir. The compost was macerated for 5 min. with the pyrophosphate solution in a Waring Blendor, and thereafter kept for 24 hours at 37° C., with intermittent stirring.

In both cases the suspensions were then centrifuged at 2,500 × g. for 45 min. and the extracts decanted. The experimental conditions and results are given in Table 4.

On drying the insoluble residue from the sulphite extraction it was found that 24·7 per cent. of the ash-free dry matter had been removed. The residue contained 89 per cent. of the original ash, 58·4 per cent. of the original nitrogen, and 66·4 per cent. of the original methoxyl.

TABLE 4

Extraction of Organic Nitrogen from Washed Compost

Extractant	*Compost: extractant ratio*	*pH of extractant*	*Final pH of extractant*	*% N extracted*
0·5 N sulphite at 102° C. . .	10·8	8·90	7·56	40·6
0·5 N pyrophosphate at 37° C. .	13·0	8·40	7·48	24·6

Isolation of the ligno-protein fraction from the compost extract

Preliminary experiments using the Sevag technique as modified by Tinsley and Zin (1954) had shown that casein, alkali wheat straw lignin, and a synthetic ligno-protein made from alkali straw lignin and casein by the method of Waksman and Iyer (1932) could be quantitatively recovered from an 0·5 N aqueous solution of either sodium sulphate or sodium sulphite at pH 7±1. The solutions for these experiments were prepared by suspending the material in the electrolyte solution, adding sufficient sodium hydroxide to bring it into solution, and then returning the pH to the required value. These experiments also showed that in Tinsley and Zin's original method considerable losses of ligno-protein occurred during the washing of the carbon tetrachloride gel carrying the ligno-protein, and that these could be prevented by washing, not with water, but with dilute electrolyte solutions. Their original gel separation technique was therefore slightly modified for the work described in this paper by using 0·1 N sodium sulphate solution as the wash liquid. Higher salt concentrations were found to be no more effective than that chosen.

The experimental procedure used in the work was as follows. Each of six 300-ml. portions of the extract was emulsified in a Waring Blendor for 2 min. with 100 ml. of carbon tetrachloride containing 0·10 g./litre of an anti-foaming agent, 'Silicone Anti-Foam A' obtained from Hopkins & Williams Ltd. After centrifuging at 1,000×g. for 5 min. the supernatant liquid was poured away from the gel and re-extracted in the same manner with a second 100-ml. portion of the carbon tetrachloride:anti-foam mixture. The extraction was continued with 100, 100, 60, and 30-ml. portions, six successive emulsifications being required to remove all the ligno-protein from the extract. From the nitrogen content of the ligno-protein free supernatant it was calculated that the original sulphite and pyrophosphate extracts contained 56·6 and 41·9 per cent. of ligno-protein nitrogen respectively. In this, as in subsequent work, nitrogen content was used as a convenient method of following ligno-protein content. That this is valid was shown when the ligno-proteins were fractionated (Section 2, *h*), the greatest range in nitrogen content being from 4·06 to 3·44 per cent.

The combined gels were stirred in the Blendor with 1,800 ml. of 0·1 N sodium sulphate, centrifuged, and the supernatant liquid, which had redissolved much ligno-protein, re-extracted with carbon tetrachloride as before until no more gel was obtained. This gel was added to

that already washed, and the whole rewashed a second time with 1,800 ml. of the sulphate solution. The supernatant obtained was re-extracted as before and the gel added to that previously obtained. Thus the gel which originally contained about 475 ml. of the aqueous phase was effectively washed with two 1,800-ml. portions of 0·5 N sodium sulphate so that about 1·2 per cent. of the non-ligno-protein nitrogen was present in the final washed gel, compared with about 25 per cent. in the unwashed gel.

Extraction of ligno-protein from the carbon tetrachloride gel

The washed gel was stirred in the Waring Blendor and centrifuged. A large portion of the gel was broken by this method and the free carbon tetrachloride poured off. The remaining gel was extracted with two successive 500-ml. portions of water. A small amount of gel still remained, and this, after centrifuging, was frozen overnight and the liberated carbon tetrachloride poured off. The residue was taken up in 150 ml. of water, the pH adjusted to neutrality, and the remaining carbon tetrachloride removed under reduced presure at 37° C. The various aqueous ligno-protein solutions were combined. The nitrogen in the combined extract amounted to 99 per cent. of that originally removed by the gel from the pyrophosphate extract, and 98 per cent. of that in the sulphite gel.

Precipitation of the ligno-proteins with acid

The ligno-protein solution was made 0·25 N with respect to sodium chloride and sufficient hydrochloric acid added to bring the pH within the region 1·6–1·8. The resulting suspension was centrifuged, the supernatant discarded, and the precipitate shaken up with 300 ml. of 0·25 N sodium chloride. This suspension was brought within the pH range 5·1–5·3 by cautious addition of 0·25 N sodium hydroxide and the acid precipitation then repeated twice more. After the last precipitation the material was resuspended in water instead of sodium-chloride solution and the total volume made up to 250 ml. the pH having been adjusted to approximately 5. In the case of L.P.P. the recovery of nitrogen from the previous stage was 89 per cent., in the case of L.P.S. 88 per cent.

De-ionization of the ligno-protein solutions

The ligno-protein solutions were de-ionized by treating them with a mixture of two parts of a weakly basic ion-exchange resin (Amberlite IR4B OH) in the basic form and one part of a strongly acidic resin (Zeocarb 225) in the hydrogen form. Exploratory experiments had shown that losses of nitrogen were greater when a strongly basic resin such as Deacidite FF was used. In addition it was desired to minimize exposure of the ligno-proteins to alkaline conditions.

The demineralizations were carried out by mixing the ligno-protein solution with an equal volume of resin mixture. This was stirred for 20 min., filtered, the resin washed, and the filtrate and washings run through a column of the mixed resins 40 cm. long and 2·5 cm. in

diameter. Water was then run through the column until no more colour was washed out and the effluent concentrated to 150 ml. under reduced pressure at 37° C. The recovery of nitrogen on de-ionization was 91 per cent. for L.P.P. and 94 per cent. for L.P.S. The concentrated L.P.P. solution contained 1·364 mg. of nitrogen per ml. and that of L.P.S. 1·413 mg. of nitrogen per ml. Most of the subsequent work was carried out on these solutions, only a small portion being freeze-dried.

Freeze-drying of the de-ionized L.P. solutions

Fifteen-millilitre portions of the concentrated de-ionized ligno-protein solutions were freeze-dried for 12 hours at a final pressure of 0·01–0·03 mm. of mercury. The ligno-proteins were obtained as very pale brown flakes, that from the pyrophosphate extract being particularly light and fluffy.

The overall yield of dry pyrophosphate-extracted ligno-protein from dry washed compost was 4·54 per cent.; it contained 7·84 per cent. of the nitrogen in the original washed compost. For the sulphite-extracted ligno-protein the corresponding figures were 11·3 per cent. and 18·3 per cent.

Section 2

Characterization of Ligno-proteins isolated from Compost

(*a*) *Elemental composition*

The elemental composition (and methoxyl content) of L.P.S. and L.P.P. are given in Table 5.

Table 5

Percentage Composition of Ligno-proteins

	L.P.P.	*L.P.S.*
Total ash .	4·89	3·68
SiO_2 . .	3·3	2·3
C . .	49·0	49·3
H . .	6·1	5·5
N . .	4·26	4·08
S . .	0·86	1·86
OMe . .	6·21	7·10

All expressed as per cent. oven-dry material.

(*b*) *Titration curves of L.P.P. and L.P.S.*

The base exchange capacity is a recognized method of characterizing 'humic' material, and may be determined by measuring the titration curve.

The presence of free basic groups in soil organic matter is a subject of much debate (Sowden, 1957) and it was thought worth while to see if they were present in L.P.S. and L.P.P. To do this the influence of formaldehyde (French and Edsall, 1945), and of electrolyte (Steinhardt and Zaiser, 1955), on the titration curves was investigated.

The titration curves were determined by taking 2 ml. aliquots of the de-ionized ligno-protein solution, making up to 10 ml. with distilled water, and titrating against 0·02 N sodium hydroxide using a glass electrode pH meter. When the titration was carried out in the presence of sodium chloride the undiluted ligno-protein was brought to pH $4{\cdot}5 \pm 0{\cdot}2$ with the standard alkali, the required amount of sodium chloride added, and the whole made up to 10 ml. with water. In the formaldehyde titration 2 ml. of a 10 per cent. formaldehyde solution was added and the final volume again made up to 10 ml. The solution was stirred by a slow stream of nitrogen, a procedure which also removed dissolved carbon dioxide. The titration curves are given in Figs. 1 and 2. The pH drift was negligible in all cases.

From the titration curves it can be seen that the addition of electrolyte increases the base-binding capacity of the ligno-proteins over the whole pH range investigated. This indicates that the isoionic point, if one exists, is at a pH below 3·5, in accord with the preponderance of acidic groups in these materials.

L.P.S. has a greater base-binding capacity than L.P.P. The cation-exchange capacity at pH 7 in the presence of 0·5 N sodium chloride is 126·8 m.e. of base/100g. dry L.P.P. and 166·5 m.e. base/100g. dry L.P.S. In calling these figures the cation exchange capacity it is assumed that all exchangeable cations were removed during de-ionization and that all the added sodium is exchangeable with N ammonium acetate at pH 7.

The de-ionized solution of L.P.S. is much more strongly acid (pH 2·71) than that of L.P.P. (pH 3·21). This and the greater base-binding capacity suggest the presence of strongly acid groups in L.P.S. that are absent in L.P.P. From the method of preparation it is probable that these are sulphonic groups. The higher sulphur content of L.P.S. (Table 5) is in accord with this theory.

The titration curves with and without formaldehyde indicate the presence of basic amino groups in small amount. These were determined by formol titration, carried out by a slight modification of the procedure recommended by French and Edsall (1945) for the determination of free side-chain amino groups in proteins. The ligno-proteins, about 150 mg. in 10 ml. of 0·5 N sodium-chloride solution, were brought to pH 8·50 with sodium hydroxide. Formaldehyde was added to bring the concentration to 2·5 per cent. (larger quantities did not significantly change the result) and the pH returned to 8·50 with 0·01 N sodium hydroxide. By this procedure free side-chain amino groups belonging to lysine or arginine are titrated but not α-amino-acid end-groups. It was found that 2·83 per cent. of the L.P.P. nitrogen was in the form of such basic groups and 2·80 per cent. in the case of L.P.S.

(*c*) *Acid hydrolysis of L.P.P. and L.P.S.*

The de-ionized ligno-protein solutions were refluxed for 8 hours with 6 N hydrochloric acid at an acid : ligno-protein ratio of about 300. This wide ratio was chosen to minimize humin formation, an experiment with casein having shown that no humin was precipitated at this ratio. The α-amino-acid concentration in the hydrolysate was determined by the

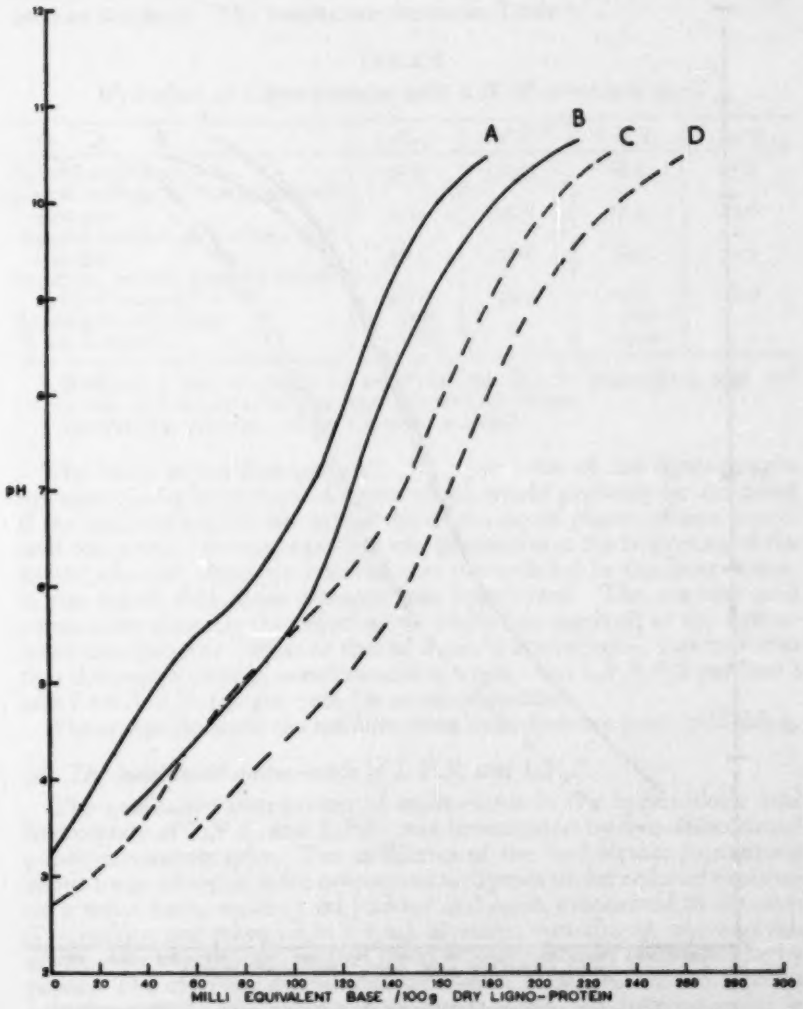

FIG. 1. Titration curves of ligno-proteins.

L.P.P. ————
L.P.S. - - - - -

A. Titration curve of L.P.P. in the absence of electrolytes.
B. Titration curve of L.P.P. in the presence of 0·5 N sodium chloride.
C. Titration curve of L.P.S. in the absence of electrolytes.
D. Titration curve of L.P.S. in the presence of 0·5 N sodium chloride.

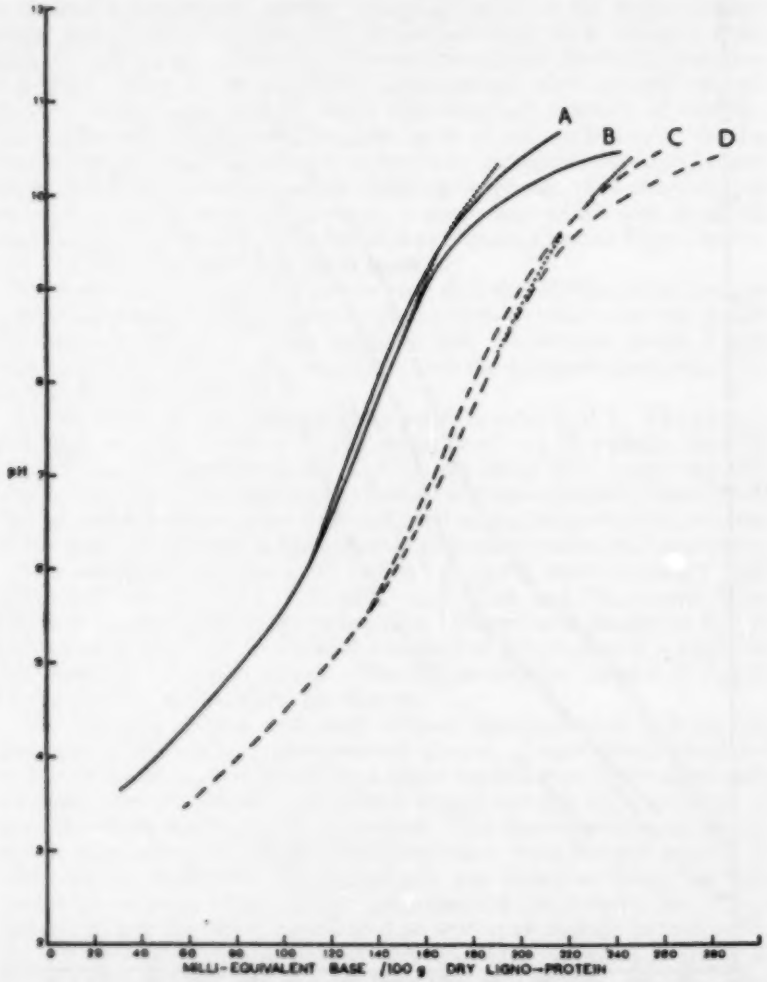

FIG. 2. The effect of formaldehyde on the titration curves of ligno-proteins.

L.P.P. ———
L.P.S. – – – –
Correction for formaldehyde blank. .....

A. Titration curve of L.P.P. in the absence of formaldehyde.
B. Titration curve of L.P.P. in the presence of formaldehyde.
C. Titration curve of L.P.S. in the absence of formaldehyde.
D. Titration curve of L.P.S. in the presence of formaldehyde.

All titrations carried out in the presence of 0·5 N sodium chloride.

colorimetric ninhydrin method of Moore and Stein (1948), glycine being used as standard. The results are shown in Table 6.

TABLE 6

Hydrolysis of Ligno-proteins with 6 N Hydrochloric Acid

	L.P.P.	*L.P.P.**	*L.P.S.*	*Casein*
% nitrogen hydrolysed	74·6	79·4	85·2	98·8
α-amino nitrogen as % of hydrolysed nitrogen	75·2	76·8	68·1	73·6
α-amino nitrogen as % of total L.P. nitrogen	56·1	61·0	58·0	72·7
Insoluble residue from hydrolysis as % of original L.P.	57·1	51·3	61·5	0·0
% nitrogen in residue†	1·96	..	1·71	..
% ash in residue	0·77	..	0·76	..

* Hydrolysed with a mixture of equal volumes of 6 N hydrochloric acid and 98 per cent. formic acid at an acid : ligno-protein ratio of 300.

† Expressed as per cent. ash-free oven-dry material.

The table shows that upwards of 75 per cent. of the ligno-protein nitrogen can be hydrolysed, a figure which would probably be increased if the hydrolysis could be carried out in the liquid phase. When formic acid was present the ligno-protein was in solution at the beginning of the hydrolysis and, although material was precipitated in the later stages, it was found that more nitrogen was hydrolysed. The α-amino-acid content (as given by the colorimetric ninhydrin method) of the hydrolysed nitrogen was similar to that of a casein hydrolysate; this indicates that the overall yield of α-amino-acid nitrogen from L.P.S. (58 per cent.) and from L.P.P. (56 per cent.) is an underestimate.

The compositions of the residues from hydrolysis are given in Table 9.

(*d*) *The constituent amino-acids of L.P.S. and L.P.P.*

The qualitative distribution of amino-acids in the hydrochloric acid hydrolysate of L.P.S. and L.P.P. was investigated by two-dimensional paper chromatography. Ten millilitres of the hydrolysate (containing about 1 mg. nitrogen) were evaporated to dryness under reduced pressure on a water bath, water (5 ml.) added and again evaporated to dryness. The residue was taken up in 1·5 ml. of water, centrifuged, and 0·04 ml. of the clear supernatant spotted on to Whatman No. 1 chromatography paper. The chromatograms were developed using the solvent systems introduced by Wolfe (1957) and the amino-acids revealed by dipping in a 0·2 per cent. solution of ninhydrin in acetone. The following amino-acids were found in L.P.P., the intensity of the spots being graded + to ++++. Cysteic acid (+), aspartic acid (++++), glutamic acid (++++), lysine (+++), arginine (+++), glycine (++++), histidine (+), serine (++++), alanine (++++), tyrosine (+), proline (+), valine (++), threonine (+++), isoleucine (++), leucine (++), phenylalanine (+), unidentified (+). Cysteic acid was graded (++) in the L.P.S. hydrolysate but otherwise the chromatograms were

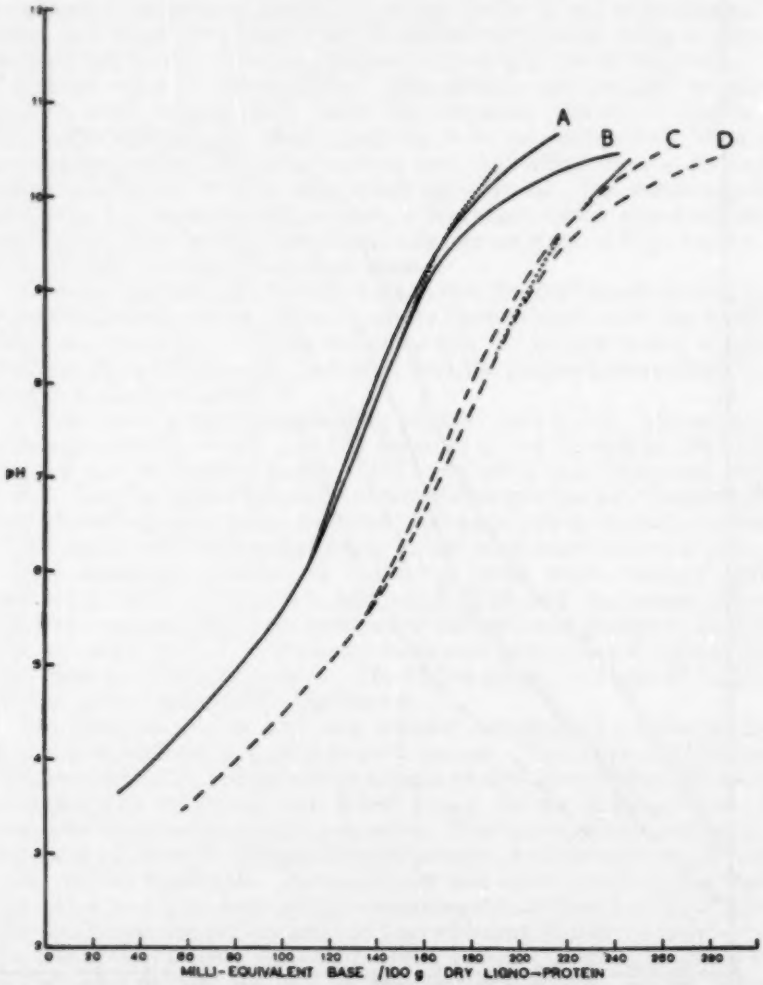

FIG. 2. The effect of formaldehyde on the titration curves of ligno-proteins.

L.P.P. ————
L.P.S. – – – – –
Correction for formaldehyde blank. .....

A. Titration curve of L.P.P. in the absence of formaldehyde.
B. Titration curve of L.P.P. in the presence of formaldehyde.
C. Titration curve of L.P.S. in the absence of formaldehyde.
D. Titration curve of L.P.S. in the presence of formaldehyde.

All titrations carried out in the presence of 0·5 N sodium chloride.

colorimetric ninhydrin method of Moore and Stein (1948), glycine being used as standard. The results are shown in Table 6.

TABLE 6

Hydrolysis of Ligno-proteins with 6 N Hydrochloric Acid

	L.P.P.	*L.P.P.**	*L.P.S.*	*Casein*
% nitrogen hydrolysed	74·6	79·4	85·2	98·8
α-amino nitrogen as % of hydrolysed nitrogen	75·2	76·8	68·1	73·6
α-amino nitrogen as % of total L.P. nitrogen	56·1	61·0	58·0	72·7
Insoluble residue from hydrolysis as % of original L.P.	57·1	51·3	61·5	0·0
% nitrogen in residue†	1·96	..	1·71	..
% ash in residue	0·77	..	0·76	..

* Hydrolysed with a mixture of equal volumes of 6 N hydrochloric acid and 98 per cent. formic acid at an acid : ligno-protein ratio of 300.

† Expressed as per cent. ash-free oven-dry material.

The table shows that upwards of 75 per cent. of the ligno-protein nitrogen can be hydrolysed, a figure which would probably be increased if the hydrolysis could be carried out in the liquid phase. When formic acid was present the ligno-protein was in solution at the beginning of the hydrolysis and, although material was precipitated in the later stages, it was found that more nitrogen was hydrolysed. The α-amino-acid content (as given by the colorimetric ninhydrin method) of the hydrolysed nitrogen was similar to that of a casein hydrolysate; this indicates that the overall yield of α-amino-acid nitrogen from L.P.S. (58 per cent.) and from L.P.P. (56 per cent.) is an underestimate.

The compositions of the residues from hydrolysis are given in Table 9.

(d) The constituent amino-acids of L.P.S. and L.P.P.

The qualitative distribution of amino-acids in the hydrochloric acid hydrolysate of L.P.S. and L.P.P. was investigated by two-dimensional paper chromatography. Ten millilitres of the hydrolysate (containing about 1 mg. nitrogen) were evaporated to dryness under reduced pressure on a water bath, water (5 ml.) added and again evaporated to dryness. The residue was taken up in 1·5 ml. of water, centrifuged, and 0·04 ml. of the clear supernatant spotted on to Whatman No. 1 chromatography paper. The chromatograms were developed using the solvent systems introduced by Wolfe (1957) and the amino-acids revealed by dipping in a 0·2 per cent. solution of ninhydrin in acetone. The following amino-acids were found in L.P.P., the intensity of the spots being graded + to ++++. Cysteic acid (+), aspartic acid (++++), glutamic acid (++++), lysine (+++), arginine (+++), glycine (++++), histidine (+), serine (++++), alanine (++++), tyrosine (+), proline (+), valine (++), threonine (+++), isoleucine (++), leucine (++), phenylalanine (+), unidentified (+). Cysteic acid was graded (++) in the L.P.S. hydrolysate but otherwise the chromatograms were

identical. Methionine could not be detected as it is not separated from glycine with the solvents system used; nor is its sulphone resolved from valine. A chromatogram dipped in 0·1 per cent. isatin in acetone confirmed the presence of proline and the absence of hydroxy-proline.

(*e*) *Alkaline hydrolysis of L.P.S. and L.P.P.*

When proteins are hydrolysed with alkali no humin is formed, although extensive decomposition and racemization of the amino-acids occurs. Experiments on an alkali wheat straw lignin, to be described in Part II, showed that, provided oxygen was excluded, the lignin was substantially unaltered by boiling for 3 hours with 2 N sodium hydroxide. Alkaline hydrolysis seemed therefore to offer an alternative to acid hydrolysis in the examination of the unhydrolysable residue. The de-ionized ligno-protein solution (15 ml.) was refluxed for 3 hours with 5 N sodium hydroxide (10 ml.) in an atmosphere of nitrogen. When cool, 5 N hydrochloric acid (12 ml.) was added, the precipitate centrifuged down, washed twice with 2 N sodium chloride, and dissolved in sufficient 0·2 N sodium hydroxide to bring the pH to 8·0. Part of the material failed to dissolve under this treatment: it was removed by centrifuging and shown to contain 70–80 per cent. silica. The supernatant was dialysed against distilled water for 16 hours and then run through a de-ionizing column of the type used in the preparation of the ligno-proteins. The eluate was concentrated under reduced pressure to about 10 ml. and then dried in a silica dish under an infra-red lamp. Table 7 gives the results.

TABLE 7

Hydrolysis of Ligno-proteins with 2 N Sodium Hydroxide

	L.P.P.	*L.P.S.*
Unhydrolysed residue as % of original L.P.	40·6	37·7
% ash in residue	3·23	3·50
% nitrogen in residue*	2·35	2·09
% methoxyl in residue*	9·43	10·02

* Expressed as per cent. ash-free oven-dry material.

Less unhydrolysed material is obtained with alkali than with acid. This is partly due to humin formation (the acid residues were much darker in colour than the alkaline ones) and partly because of greater losses in the isolation of the residue from alkaline hydrolysis. The composition of these residues is given in Table 9.

(*f*) *Reaction of L.P.P. and L.P.S. with 2:4-dinitrofluorobenzene*

2:4-dinitrofluorobenzene was introduced by Sanger (1945) for the detection and estimation of α-amino end-groups in proteins. It can also be used to detect peptide-bound lysine, since in this case the ε-amino group is free to react with the reagent although the α-amino group is not.

To 1 ml. of the de-ionized ligno-protein solution containing 0·025 g. of sodium bicarbonate was added 2 ml. of a 2·5 per cent. solution of F.D.N.B. in ethanol. The suspension was shaken at room temperature for 2 hours and then brought to pH 2 with hydrochloric acid. The

precipitate was removed by centrifuging, washed successively with water, ethanol, and ether, giving 0·024 g. of the F.D.N.B. ligno-protein complex from both L.P.S. and L.P.P. The complex (0·020 g.) was hydrolysed with constant B.P. hydrochloric acid (2 ml.) for 16 hours in a sealed tube at 105° C. The hydrolysate was diluted, insoluble material centrifuged off, and the supernatant extracted exhaustively with ether. Hydrochloric acid was removed from the aqueous phase under reduced pressure, the residue made up to 2 ml. with water, and 0·04-ml. portions spotted on Whatman No. 4 paper. The method developed by Lowther and Blackburn (1951) for the chromatographic separation of amino-acid derivatives of F.D.N.B. was used. No distinct spots were obtained from the ethereal extract, but a single strong yellow spot was obtained from the water-soluble part of the hydrolysate with both L.P.S. and L.P.P. These spots were identical in R.F. value and in their colour reaction with ninhydrin with a sample of ε-N-2:4-dinitrophenyl-1-lysine prepared by hydrolysing the F.D.N.B. derivative of trypsin.

It follows that both ligno-proteins contain free lysine ε-amino groups, but neither contains any specific end-group amino-acid.

(*g*) *Carbohydrate material in L.P.S. and L.P.P.*

Both L.P.S. and L.P.P. contain a small proportion of carbohydrate material. A rough estimate of the quantity was obtained by hydrolysing the ligno-proteins with 2 N sulphuric acid for 3 hours and determining the reducing sugars in the hydrolysate by the anthrone method (Morris, 1948). It was found that between 3 and 6 per cent. of L.P.S. could be hydrolysed to reducing sugars (calculated as glucose) and that for L.P.P. the corresponding figure was between 5 and 8 per cent.

(*h*) *Fractionation of ligno-proteins*

A fractional precipitation of the ligno-proteins was carried out in order to obtain some idea of the heterogeneity of the preparations. Using ammonium sulphate as precipitant, it was found that L.P.S. was precipitated over a much wider range of salt concentrations than L.P.P. The least soluble fraction of L.P.S. contained 4·06 per cent. nitrogen and 5·59 per cent. methoxyl, the most soluble 3·44 per cent. nitrogen and 7·46 per cent. methoxyl. No such fractionation into high nitrogen:low methoxyl and low nitrogen:high methoxyl was obtained with L.P.P. It appears that the pyrophosphate ligno-protein is a more homogeneous material than that from the sulphite extract.

(*i*) *Enzymic hydrolysis of the ligno-protein*

If the protein-lignin reaction only takes place at a small number of sites on the protein it is possible that much of the protein is unprotected to hydrolysis by proteolytic enzymes.

In order to see if this was so and thereby obtain a 'lignin' fraction from the ligno-proteins, the hydrolysis of L.P.P. and L.P.S. with papain, trypsin, and chymotrypsin was investigated. These particular proteolytic enzymes were chosen since trypsin requires that the carbonyl group of the peptide link being hydrolysed belong to either lysine or arginine,

and chymotrypsin does not. Since it has been suggested (Waksman, 1938) that proteins are likely to react with lignin through the basic side groups of these amino-acids it was thought possible that trypsin and chymotrypsin would behave differently towards ligno-proteins. Papain was chosen as a 'broad spectrum' proteolytic enzyme capable of attacking most peptide bonds.

Crystalline trypsin and chymotrypsin, obtained from Armour & Co., Inc., were used as a solution of the enzyme in water. The papain was prepared from dried papaya latex (supplied by Light & Co., Ltd.) by the method of Kimmel and Smith (1954). However, instead of precipitating the papain with ammonium sulphate and then crystallizing as described by these authors the active extract was dialysed until free from cysteine, made 0·1 M with phosphate buffer at pH 7·1, and stored at −20° C. This preparation therefore contained both papain and chymopapain, a proteolytic enzyme very similar to papain in action. When required for use, 1 ml. of this solution (containing 3·69 mg. nitrogen/ml.), 2·5 ml. of 0·3 M sodium thioglycollate, and 2·5 ml. of 0·06 M ethylenediaminotetracetic acid were made up to 25 ml. with water and 2 ml. of this used for hydrolysis. This gave a thioglycollate concentration of 0·005 M and an E.D.T.A. concentration of 0·001 M in the hydrolysis. Thioglycollic acid was used as it was found to be as efficient an activator for papain as cysteine and had the advantage of not containing nitrogen.

All hydrolyses were carried out in 0·1 M phosphate buffer at pH 7·05–7·10, a pH close to the optimum for all three enzymes. The deionized ligno-protein solutions were adjusted to approximately pH 7 with sodium hydroxide, and the required amounts of disodium and monopotassium phosphate dissolved in this solution. A standard casein solution was prepared by dissolving Hammarsten casein (supplied by Hopkins & Williams, Ltd.) in the same buffer.

The reaction was followed by determining the trichloracetic acid insoluble (protein) nitrogen remaining after a given time. The hydrolyses were carried out in stoppered boiling tubes at 37° C. To a suitable aliquot of the protein solution was added sufficient buffer to bring the total volume to 10 ml., followed by 2 ml. of the enzyme solution. A 1-ml. sample was withdrawn immediately, and at suitable intervals thereafter. Then 7 ml. of 5 per cent. trichloracetic acid were immediately added to the sample and the mixture allowed to stand 1 hour before being filtered. The nitrogen content of an aliquot (usually 5 or 6 ml.) of the clear filtrate was determined by the Kjeldahl method. The nitrogen content of the first sample corresponded to the amount of T.C.A. soluble nitrogen present before hydrolysis had commenced, and was subtracted from all the others. It amounted to 7–10 per cent. of the total ligno-protein nitrogen. Where the extent of hydrolysis was slight 2-ml. samples were taken and 14 ml. of the T.C.A. solution added.

The results for the tryptic hydrolysis are shown in Fig. 3.

With these high enzyme concentrations casein was completely broken down to T.C.A. soluble material in a very short time. In the case of L.P.S. about 15 per cent. of the nitrogen was rapidly hydrolysed, followed by a slow hydrolysis of a further 5 per cent. About 5 per cent. of

L.P.P. was rapidly hydrolysed, followed by the slow hydrolysis of a further 3 per cent.

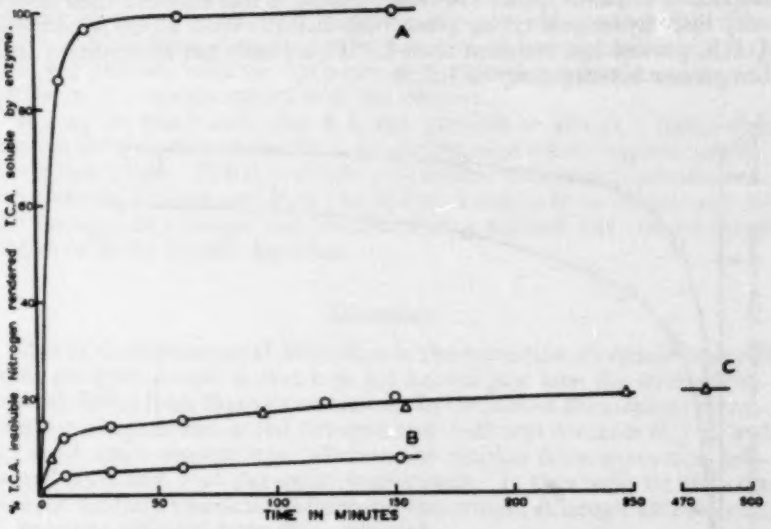

FIG. 3. Hydrolysis of ligno-proteins with trypsin.

A. Hydrolysis of casein (0·750 mg. casein nitrogen/ml.).
B. Hydrolysis of L.P.P. (0·750 mg. L.P.P. nitrogen/ml.).
C. Hydrolysis of L.P.S. (0·750 mg. L.P.S. nitrogen/ml.).

Trypsin concentration 0·0427 mg. nitrogen/ml. in all cases except those results indicated by Δ where it was 0·0175 mg. trypsin nitrogen/ml.

Similar results were obtained with the other enzymes. The results are summarized in Table 8, which gives the per cent. hydrolysis at 120 min., a time when both slow and fast hydrolysis were substantially completed at the enzyme concentration used.

TABLE 8

Per cent. of T.C.A. precipitable Nitrogen Hydrolysed to T.C.A. Soluble Nitrogen by Enzyme in 120 Minutes at 37° C.

Enzyme	*Enzymic concentration mg. N/ml.*	*Substrate*				
		L.P.P., 0·645 mg. N/ml.	*L.P.S., 0·645 mg. N/ml.*	*Casein 0·645 mg. N/ml.*	*Casein 0·645 mg. N/ml. L.P.P. 0·128 mg. N/ml.*	
Papain . .	0·0587	3·3	14·3	(93·2) 97·6	..	..
Trypsin . .	0·0320	7·8	18·8	(92·0) 98·0	(79·3)*	88·9*
Chymotrypsin	0·0244	10·0	17·8	(83·3) 91·5	(69·1)*	78·1*

Figures in parentheses give per cent. hydrolysis in 30 min.
* Calculated as per cent. T.C.A. precipitable casein nitrogen, not total T.C.A. precipitable nitrogen.

From the results given in Table 8 and from Fig. 3 it is clear that there is no significant difference between the extent of hydrolysis using trypsin or chymotrypsin. However, papain is less effective than either, very little hydrolysis taking place with L.P.P. With all three enzymes L.P.S. proved less resistant than L.P.P., a result not inconsistent with the greater heterogeneity of L.P.S.

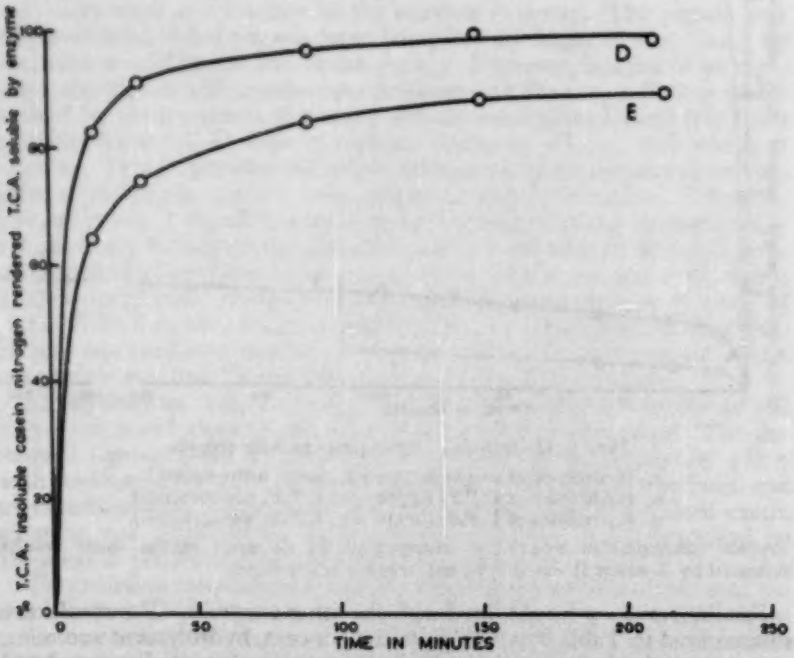

FIG. 4. Enzymic hydrolysis of casein in the presence of L.P.S.

D. Hydrolysis of casein (0·808 mg. casein nitrogen/ml.) with trypsin (0·0175 mg. trypsin nitrogen/ml.).

E. Hydrolysis of casein (0·808 mg. casein nitrogen/ml.) in the presence of L.P.S. (0·150 mg. L.P.S. nitrogen/ml.) with trypsin (0·0175 mg. trypsin nitrogen/ml.).

Nitrogen rendered T.C.A.-soluble by enzyme expressed as a percentage of the original T.C.A.-insoluble casein nitrogen.

One possible explanation for the resistance of these materials to enzymic hydrolysis is that they inactivate the enzyme. That this will only provide a partial explanation was shown by hydrolysing casein in the presence of varying quantities of ligno-protein. Some of these results are shown in Fig. 4 and some in the last column of Table 8. These results show that only partial if any inactivation of the enzyme takes place with the levels of L.P.S. used in this experiment and that the L.P.S. seemed to protect some of the casein from attack. Similar effects were found when an alkali straw lignin in phosphate buffer was used in place

of L.P.S. These experiments showed that the higher the lignin concentration the less casein hydrolysed and that doubling the enzyme concentration at the same lignin level gave a small increase in the final amount of casein hydrolysed (compare Fig. 3 in this connexion). The enzymic hydrolysis of casein in the presence of ligno-proteins is a very complex process, with the ligno-protein interacting with the casein and probably to a certain extent with the enzyme.

It may be concluded that it is not possible to obtain a lignin-rich fraction from ligno-proteins by enzymic hydrolysis with trypsin, papain, or chymotrypsin. This is in accord with earlier work on similar materials: for example, Hobson and Page (1932) found that only 10–20 per cent. of the nitrogen in a humic acid isolated from a mineral soil was rendered acid-soluble by tryptic digestion.

Discussion

One of the fundamental difficulties in the extraction of organic material from compost or soil is that it is not known just how the material extracted differs from that not extracted. In the case of the sulphite extraction the compost had initial nitrogen and methoxyl contents of 3·48 and 3·42 per cent. respectively, whereas the residue from extraction contained 2·04 and 3·46 per cent. respectively. It may well be that the residue contains unextracted ligno-protein which, although undissolved, is not very different from that extracted.

Another difficulty inherent in organic matter extractions is that reaction may take place between various fractions subsequent to their solution. For example, the lignin and protein could conceivably be dissolved independently and then react in solution. Although this possibility cannot be rigorously excluded it is most unlikely that there could be any substantial quantity of free protein after 480 days of decomposition.

A third problem in isolating organic matter is that the extractant either reacts with or catalyses changes in the material extracted. In the pyrophosphate extraction the pH was kept below 8·4 so that atmospheric oxidation (Bremner, 1950) was minimized. Oxygen uptake is probably less serious with sodium sulphite as the oxygen content of the solution would be kept very low by the sulphite ions. However, in this case there is evidence that a certain amount of sulphonation occurs, even though the pH did not fall below 7·5. The sulphonation of lignin with sodium sulphite is a slow process at pH's above 6. For example, Brauns (1952) found that high temperatures (180° C.) were needed to produce significant sulphonation of a spruce lignin. Nevertheless, the higher sulphur content, the larger cation exchange capacity, the shape of the titration curves in the pH region 3·5–2·7, and the infra-red spectrum (see Part II) all indicate the presence of sulphonic groups in L.P.S. that are absent in L.P.P. This is a serious disadvantage in the use of sodium sulphite as an extractant, particularly if lignin type materials are being investigated.

The most conclusive evidence for the presence of lignin in the un-

hydrolysable residue from both L.P.P. and L.P.S. is obtained from the infra-red spectra (see Part II). The elemental composition and methoxyl content of the insoluble residues from the hydrolysis of L.P.S. and L.P.P. are collected in Table 9, which also contains data on a sample of wheat straw lignin which had been refluxed for 4 hours with 2 N sodium hydroxide.

TABLE 9

The Elemental Composition (and Methoxyl Content) of an Alkali-treated Straw Lignin and the Residues from Alkaline and Acid Hydrolysis of L.P.P. and L.P.S.

Material hydrolysed	*Straw lignin*•	*L.P.P.*	*L.P.S.*	*L.P.P.*	*L.P.S.*
Hydrolytic conditions	2 N NaOH	2 N NaOH	2 N NaOH	6 N HCl	6 N HCl
% C	60·1	56·2	56·7	58·6	58·0
% H	5·7	6·1	6·2	5·2	5·6
% N	0·41	2·35	2·09	1·96	1·71
% OMe	16·9	9·43	10·02	8·51	8·34
% S	..	0·45	1·11	..	..

All expressed as per cent. ash-free oven-dry material.
• See Part II for a full description of this material.

The data in Table 9 are not inconsistent with the infra-red results although the carbon and methoxyl contents of the residues from hydrolysis are lower than those of the wheat straw lignin. Part of this difference will be accounted for by the higher nitrogen content of the ligno-protein derived materials. Whether or not this will explain the considerable fall in methoxyl is not clear: it is possible that a certain amount of demethylation had occurred during the rotting process.

It is clear that the bulk of the nitrogeneous part of both L.P.S. and L.P.P. is composed of α-amino-acids. The amino-acid pattern was very similar to that obtained from the hydrolysis of a wheat straw compost by Bremner (1955). His results were obtained on hydrolysis of the whole compost; this may explain the absence of amino-sugars, α : ε-diaminopimelic acid and β-alanine in the hydrolysates from the ligno-protein. It is possible, however, that the unidentified spot in the ligno-protein hydrolysate may be due to β-alanine.

The way in which the α-amino-acids are bound in the ligno-protein is much less certain, since the enzymic work failed to provide information on this point. However, infra-red studies (Part II) showed that absorption bands characteristic of the peptide link are well resolved in both L.P.P. and L.P.S. This is the only evidence that the amino-acids occur as peptide chains in the ligno-proteins. The F.D.N.B. results indicate that no one specific amino-acids occurs in the terminal position of the peptide chain, if such chains exist.

Considered as a whole, the properties of the material adsorbed on the interface justify the use of the term 'ligno-protein' although 'ligno-peptide' might be equally correct.

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REFERENCES

BLACKBURN, S., and LOWTHER, A. G. 1951. The separation of N-2:4-dinitrophenyl amino-acids on paper chromatograms. Biochem. J. **48**, 123.

BRAUNS, F. E. 1952. The Chemistry of Lignin. Academic Press, New York.

BREMNER, J. M. 1950. Some observations on the oxidation of soil organic matter in the presence of alkali. J. Soil Sci. **1**, 198.

—— 1955. Nitrogen transformations during the biological decomposition of straw composted with inorganic nitrogen. J. Agric. Sci. **45**, 469.

—— HEINTZE, S. G., LEES, H., and MANN, P. J. G. 1946. Metallo-organic complexes in soil. Nature, Lond., **158**, 790.

COULSON, C. B. 1953. Private communication.

FRENCH, D., and EDSALL J. T. 1945. The reactions of formaldehyde with amino acids and proteins. Advanc. Protein Chem. **2**, 277.

HOBSON, R. P., and PAGE, H. J. 1932. Studies on the carbon and nitrogen cycles in the soil. J. Agric. Sci. **22**, 497.

KIMMEL, J. R., and SMITH, E. L. 1954. Crystalline Papain. J. Biol. Chem., **207**, 515.

MOON, F. E., and ABOU RAYA, A. K. 1954. The lignin fraction of animal feeding-stuffs. J. Sci. Fd. Agric. **5**, 319.

MOORE, S., and STEIN, W. H. 1948. Photometric ninhydrin method for use in chromatography of amino acids. J. Biol. Chem. **176**, 367.

MORRIS, D. L. 1948. Quantitative determination of carbohydrates with Dreywood's anthrone reagent. Science, **107**, 254.

RUDLOFF, E. VON. 1957. High results in methoxyl determinations on mixtures containing polyhydric alcohols. Anal. Chim. Acta. **16**, 294.

SANGER, F. 1945. The free amino groups of insulin. Biochem. J. **39**, 507.

SEVAG, M. G., LOCKMAN, D. B., and SMOLENS, J. 1938. The isolation of the components of streptococcal nucleoproteins in serologically active form. J. Biol. Chem. **124**, 425.

SOWDEN, F. J. 1957. Note on the occurrence of amino groups in soil organic matter. Canad. J. Soil. Sci. **37**, 143.

STEINHARDT, J., and ZAISER, E. M. 1955. Hydrogen ion equilibria in native and denatured proteins. Advanc. Protein Chem. **10**, 151.

TINSLEY, J., and ZIN, M. K. 1954. The isolation of ligno-proteins from soil. Trans. V. Congr. Int. Sci. Soil, Comm. II, 342.

—— and NOWAKOWSKI, T. Z. 1959. J. Sci. Fd. Agric. **10**, 150.

VOGEL, A. I. 1951. Quantitative Inorganic Analysis, 2nd ed. Longmans, London.

WAKSMAN, S. A. 1938. Humus, 2nd ed. Williams & Wilkins, Baltimore.

—— and IYER, K. R. N. 1932. Contributions to our knowledge of the chemical nature and origin of humus. Soil Sci. **34**, 43.

WOLFE, M. 1957. The quantitative determination of amino acids by paper chromatography. Biochem. Biophys. Acta, **23**, 186.

ZIN, M. K. 1955. Thesis, University of Reading.

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STUDIES ON THE ORGANIC MATERIAL EXTRACTED FROM SOILS AND COMPOSTS

II. THE INFRA-RED SPECTRA OF LIGNO-PROTEINS ISOLATED FROM COMPOST

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Summary

The infra-red absorption spectra of the ligno-proteins described in Part I of this series of papers were examined and absorption bands characteristic of the peptide link identified.

A reference sample of lignin was prepared from wheat straw and was found to be relatively unchanged by boiling with 2 N sodium hydroxide for 4 hours in the absence of air.

The infra-red spectra of the residues from acid and alkaline hydrolysis of the ligno-proteins were found to be very similar to that of straw lignin.

THE principal difficulty in working with 'humic' colloids is in characterizing them. Infra-red spectroscopy has been introduced for this purpose (Kononowa and Beltschikowa, 1956), but owing to the great heterogeneity of the 'humic' and 'fulvic' acids examined, resolution was poor and comparatively little information could be obtained from the spectra. This was also true of the 'humic acids' isolated from a range of soils by Kumada and Aizawa (1958). However, exploratory experiments in which the spectra of ligno-proteins from soil were compared with those from compost showed that resolution was uniformly better with the latter. Infra-red spectroscopy seemed therefore a promising tool in the investigation of the compost ligno-proteins whose preparation and properties were described in Part I. The abbreviations introduced in Part I, L.P.S. for the ligno-protein isolated from the sulphite extract of compost, and L.P.P. for that isolated from the pyrophosphate extract of the same compost, are used throughout the present paper.

The aims of the work described in Part II of this paper were: (i) to obtain spectral data on L.P.P. and L.P.S. which could be compared with that of ligno-proteins from other sources; (ii) to see what information could be obtained about their structure from these data; and (iii) to examine the residues from the hydrolysis of the ligno-proteins and to see to what extent, if any, they resembled lignin from straw. There is no satisfactory way of identifying or determining lignin in decomposing plant material containing much nitrogen, and in this work the infra-red spectrum was used as the only reliable method of identifying lignin isolated from such surroundings.

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Experimental Part

For this work it was necessary to prepare a reference sample of wheat-straw lignin and to investigate its stability to alkali treatment, since some of the previously reported hydrolyses of ligno-protein were carried out under alkaline conditions (Part I).

Preparation of alkali wheat straw lignin

Straw (350 g.) was ground to pass a 0·5 mm. sieve and dewaxed by refluxing with three successive portions of a 1 : 1 mixture of benzene and acetone. The dry dewaxed straw was then boiled with four successive portions of water for periods of 1 hour, the final aqueous extract being almost colourless. It was then extracted at room temperature with 4 l. of 2 per cent. sodium hydroxide for 7 days in the absence of air. The extract was acidified, the precipitate centrifuged down, and the lignin redissolved by boiling with 250 ml. of a mixture of 9 parts ethanol, 9 parts acetone, and 2 parts water. The suspension was centrifuged, the residue re-extracted with a further 100 ml. of the solvent mixture, and the combined lignin solutions diluted with 3 l. of water containing 10 g. of sodium sulphate. The lignin was filtered off, air-dried, and purified by precipitating the dioxan-soluble part with ether as described by Brauns (1952), the final yield of dioxan-soluble material being 10·2 g. This contained 60·0 per cent. carbon, 5·7 per cent. hydrogen, 0·79 per cent. nitrogen, and 17·3 per cent. methoxyl.

Stability of wheat straw lignin to alkaline hydrolysis

A portion of the dioxan-soluble material (1 g.) was refluxed for 4 hours with 2 N sodium hydroxide under nitrogen. The solution was acidified, the precipitate dried, dissolved in dioxan, and precipitated with ether as before to give 0·84 g. of a dioxan-soluble material which contained 60·1 per cent. carbon, 5·7 per cent. hydrogen, 0·41 per cent. nitrogen, and 16·9 per cent. methoxyl.

Infra-red measurements

The spectra were obtained with a double beam Grubb Parsons S3A infra-red spectrometer fitted with a rocksalt prism. The samples (approximately 1·5 mg.) were ground with 200 mg. of potassium bromide for 2 min. in a ball-mill and the mixture pressed into discs which were placed in one beam of the spectrometer, a second disc of pure potassium bromide being placed in the comparison beam.

The particle size of materials which had been prepared by either freeze drying (spectra C and D) or precipitation from dioxan (A and B) was very small and the samples were added directly to the potassium bromide in the mill. Materials that had been obtained by evaporating aqueous solutions (H and E) or as residues from acid hydrolysis (F and G) were given a preliminary grinding in an agate mortar. Even with this additional grinding the particle sizes were considerably larger than those of the precipitated or freeze-dried materials, as shown by the increase in scattering at the shorter wavelengths.

Results and Discussion

The spectrum of straw lignin

Fig. 1 shows the spectrum of wheat straw lignin before and after refluxing with 2 N alkali (curves A and B respectively); the only significant change being the removal of the weak bands at 1,650 cm.$^{-1}$ and 1,360

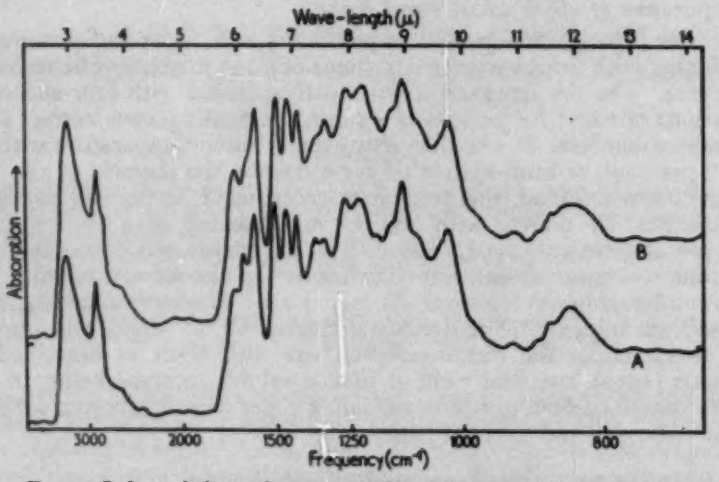

FIG. 1. Infra-red absorption spectra of lignin. A, straw lignin; B, straw lignin after treatment with boiling 2 N sodium hydroxide for 4 hours.

cm.$^{-1}$. The first of these is almost certainly connected with the removal of protein or peptide nitrogen during hydrolysis. Proteins and peptides show an intense band near 1,650 cm.$^{-1}$ (Bellamy, 1954), a band which would disappear on hydrolysis with hot alkali. Results obtained in the course of other work on an alkali spruce lignin containing 0·08 per cent. of nitrogen lend additional support to this assignment. The intensity of the 1,650 cm.$^{-1}$ band became progressively less in three fractions which were successively precipitated by benzene from a dioxane solution of the lignin. The nitrogen contents of the fractions were found to be 0·21 per cent., 0·10 per cent., and 0·02 per cent. In the sample containing 0·02 per cent. nitrogen the 1,650 cm.$^{-1}$ band was virtually absent.

The analytical composition and the infra-red spectrum of the lignin before and after hydrolysis show that it is substantially unaffected by alkali under the conditions used in Part I for the hydrolysis of lignoproteins. Further experiments showed that, if air was not excluded during alkaline hydrolysis, a darker product was recovered with a less well resolved spectrum than that of the original lignin.

The spectra of L.P.S. and L.P.P.

Fig. 2 shows the spectrum of L.P.S. (C), and of L.P.P. (D). The amide I and amide II bands can be identified at 1,650 cm.$^{-1}$ and 1,510 cm.$^{-1}$ respectively. These bands are characteristic of the peptide

link and are present as intense bands in the infra-red spectra of proteins and polypeptides. Two bands, one near 1,600 cm.$^{-1}$ and the other near 1,500 cm.$^{-1}$, are characteristic of aromatic ring systems (Bellamy, 1954) and it is possible that the inflection at 1,600 cm.$^{-1}$ in C and D is due to the

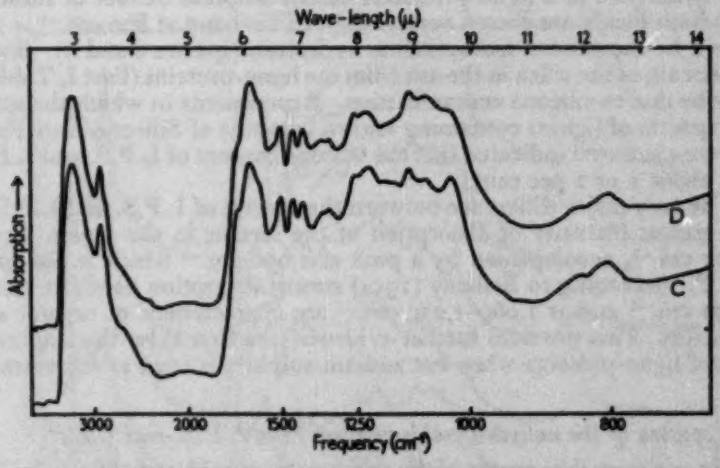

FIG. 2. Infra-red absorption spectra of ligno-proteins from compost. C, L.P.S; D, L.P.P.

former. The unusually low frequency of the amide II band (Bellamy, 1954, places it at about 1,550 cm.$^{-1}$) is probably due to a superposition of this band and the 1,500 cm.$^{-1}$ aromatic band. Confirmation of these assignments was provided by the disappearance of the amide I band on hydrolysis with the concomitant appearance of free α-amino acids in the hydrolysate (see Part I). With the removal of the amide bands, both aromatic bands are clearly shown in the spectra of the residues from hydrolysis of the ligno-proteins (see Fig. 3).

The inflection at 1,700 cm.$^{-1}$ cannot be identified with such certainty. From the cation-exchange capacity (Part I), it is probable that at least part of this inflection is due to unionized carboxyl groups, but several other groups, for example aryl ketones, could contribute to its intensity.

The weak band at 840 cm.$^{-1}$ in the spectra of L.P.P. and L.P.S. appears at a greater intensity in both lignin and the residues from hydrolysis. Lignin is known to contain aromatic rings with 1:3:4:5 and 1:3:4 substitution (Alder and Lindgren, 1952). The two vicinal hydrogen atoms in rings with 1:3:4 substitution give rise to a strong absorption band near 840 cm.$^{-1}$ (Bellamy, 1954), and it is probable that the band at this frequency in both lignin and the ligno-proteins is due to this system.

The band at 805 cm.$^{-1}$ is almost certainly due to the Si-CH_3 vibration, since it only appeared when Silicone Anti-Foam A, which contains a dimethyl silicone, was used as anti-foaming agent in the isolation of the ligno-proteins (Part I). Samples prepared using capryl alcohol as anti-foaming agent did not show this band in their spectra. Bellamy (1954)

lists 1,259 cm.$^{-1}$ and about 800 cm.$^{-1}$ as characteristic absorption frequencies of the Si-CH_3 group. In cases where larger amounts of Silicone Anti-Foam A were carried by the ligno-protein or lignin (for example Spectrum 1, Fig. 3, which is that of a 'lignin' obtained by alkaline hydrolysis of a ligno-protein from the sulphite extract of meadow soil) both bands are shown very clearly. This band at 800 cm.$^{-1}$ is also shown by the residue from alkaline hydrolysis (spectra E and H). Some, but not all, of the silica in the ash from the ligno-proteins (Part I, Table 6) may be due to silicone contamination. Experiments in which the infra-red spectra of lignins containing known amounts of Silicone Anti-Foam A were measured indicated that the silicone content of L.P.S. and L.P.P. was about 1 or 2 per cent.

The only major difference between the spectra of L.P.S. and L.P.P. is the greater intensity of absorption of the former in the region 1,250–1,150 cm.$^{-1}$, accompanied by a peak at 1,036 cm.$^{-1}$ which is absent in L.P.P. According to Bellamy (1954) strong absorption bands at 1,210–1,150 cm.$^{-1}$ and at 1,060–1,030 cm.$^{-1}$ are characteristic of organic sulphonates. This provides further evidence (see Part I) for the sulphonation of ligno-proteins when hot sodium sulphite is used as extractant.

The spectra of the unhydrolysable residues from L.P.S. and L.P.P.

Fig. 3 shows the spectra of the residues from acid and alkaline hydrolysis of L.P.S. and L.P.P. (E, F, G, and H) together with that of the straw lignin which had been treated with boiling 2 N sodium hydroxide (B).

Comparing first spectrum B, that of the reference lignin, and E, that of the residue from the alkaline hydrolysis of L.P.P., it is clear that they are very similar. All the main absorption bands in B are present in E although they are less clearly defined, presumably due to the greater heterogeneity of the sample. The most important differences are (*a*) the scattering effects shown in E at short wave-lengths, due to the larger particle size of the sample, (*b*), a band at about 800 cm.$^{-1}$ in E probably caused by silicone contamination, (*c*), the higher intensity of E in the 1,050–1,100 cm.$^{-1}$ region, and (*d*), the higher intensity of E between 1,600 cm.$^{-1}$ and 1,700 cm.$^{-1}$, presumably due to the remnants of the amide I band (the sample contained 2·35 per cent. of nitrogen).

When the spectrum of the residue from acid hydrolysis from L.P.P. (F) is contrasted with that from alkaline hydrolysis (E) a peak at 1,704 cm.$^{-1}$ is clearly revealed in the former. The inflection between the maxima at 1,704 cm.$^{-1}$ and at 1,600 cm.$^{-1}$ is again almost certainly due to remnants of the amide I band resulting from incomplete hydrolysis. Another feature of the acid-hydrolysed material is the absence of a clearly defined 'Silicone Anti-Foam A' band at 800 cm.$^{-1}$; the silicone appears to have been eliminated during hydrolysis. The spectra of the residues from acid (G) and alkaline hydrolysis (H) of L.P.S. differ from each other in an exactly similar manner. The band at 1,704 cm.$^{-1}$ is resolved in the former and the silicone band does not appear. The overall similarity of both G and H to the reference lignin is again clear. The only significant difference between the spectra of the residues from

L.P.P. and those of the residues from L.P.S. is the presence of a maximum at 1,030 cm.$^{-1}$ in the latter. A band at this position appears in the spectrum of straw lignin. It is not clear whether this is because the

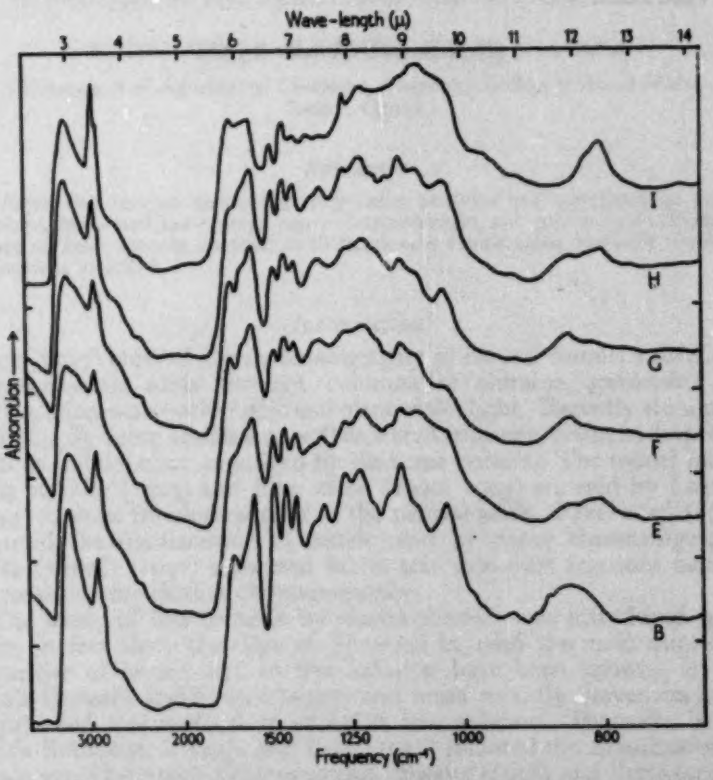

FIG. 3. Comparison between the infra-red absorption spectra of the residues from acid and alkaline hydrolysis of ligno-proteins and that of straw lignin. B, straw lignin after treatment with boiling 2 N sodium hydroxide for 4 hours; E, residue from alkaline hydrolysis of L.P.P.; F, residue from acid hydrolysis of L.P.P.; G, residue from acid hydrolysis of L.P.S.; H, residue from alkaline hydrolysis of L.P.S.; I, residue from alkaline hydrolysis of a ligno-protein from a mineral soil.

material derived from L.P.S. is more similar to straw lignin than that from L.P.P. or whether this band is due to the sulphonic group. In view of the higher sulphur content of the former (see Part I, Table 10) the presence of sulphonic groups is the more likely of the two.

REFERENCES

BELLAMY, L. J. 1954. The Infra-red Spectra of Complex Molecules. Methuen, London.

BRAUNS, F. E. 1952. The Chemistry of Lignin. Academic Press, New York.
KONONOWA, M. M., and BELTSCHIKOWA, N. P. 1956. Humus der Böden der U.d.S.S.R. Rapp. VI. Congr. Int. Sci. Sol., Comm. **2**, 557.
KUMADA, K., and AIZAWA, K. 1958. The infra-red spectra of humic acids. Soil Plant Fd. **3**, 152.

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HUMIC-ACID INVESTIGATIONS

II. STUDIES IN THE FRACTIONATION OF HUMIC ACIDS*

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Summary

Paper and column chromatography using partition and ion-exchange conditions, high- and low-voltage paper electrophoresis, and gelatine-gel diffusion have all been used in an attempt to fractionate humic acids, but only limited success is recorded.

Introduction

Hock (1937) studied the chromatography of natural humic, fulvic, and hymatomelanic acids through columns of alumina, examining for fractionation with both visible and ultra-violet light. Recently Kononova *et al.* (1958), using alumina as well as starch columns, claim an improvement in fractionation as judged by the same criteria. The model humic acids of Eller (1923) and Eller *et al.* (1920, 1923) are said by Laatsch (1944) to show fractions similar to the natural acids. Pavel *et al.* (1953) reported the fractionation of humic acid by paper chromatography, while Forsyth (1947) separated fulvic acid into four fractions using a charcoal pad for elution chromatography.

The study of humic acids by electrophoresis was introduced quite early, in fact since the days of Sprengel in 1826 the main migration properties of humic acid in free solution have been known. In the 1920's Ostwald and Steiner (1925) and more recently Stevenson *et al.* (1952) used this method of study in free solution. However, in the 1950's Robinson, Martin, and Page (1951) initiated the examination of humic acids by paper electrophoresis. Swaby (1958) and Bremner and Arnold (1952) found only one component by this means whilst others claim more than one component (Pavel *et al.*, 1953; Welte, 1955; Scheffer *et al.*, 1955), e.g. Pavel *et al.* (1953) observed several fluorescent areas on paper electrophoretograms. It was observed too that polymers produced by the oxidation of polyphenols (Eller and Koch, 1920) showed similar patterns on paper (Scheffer *et al.* 1955). Continuous paper electrophoresis failed to produce any significantly different fractionation of the humic acids as far as could be judged from the amino-acids of the fractions (Swaby, 1958). Pavel (1958) has found that chromatography and electrophoresis generally have failed to produce really effective separation.

* Part I. R. I. Davies, C. B. Coulson, and C. Luna, Chem. & Ind., 1957, p. 1544.

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Experimental

Humic acid and lignin samples

Peats from an upland acidic site at Gilar, Pentrevoelas, North Wales, and a clay fraction from the College Farm, Aber, North Wales, were extracted for humic acid by the neutral-pyrophosphate method of Bremner and Lees (1949), but the final treatment by alcohol and benzene (Bremner, 1955) was omitted. Instead the humic acids were precipitated a number of times from neutral pyrophosphate solution. The clay fraction (<0·001 mm.) was prepared by water dispersion of clay of the Aber series, decanting a 10-cm. column after 16 hours' standing. After separating in a Sharples centrifuge, the clay was dried at 35°.

Two other humic acids were used, one a commercial sample from a bituminous deposit (Lights & Co.) and the other a sample from peat by high-temperature alkaline extraction under an atmosphere of nitrogen (kindly supplied by Dr. Diarmuid Murphy, Chemistry Department, University College, Dublin).

Two commercial lignins were examined: Indulin A (kindly supplied by the West Virginia Paper & Pulp Co.) and Meadol (a soda lignin kindly supplied by the Mead Corporation, Ohio), and also a sulphite liquor (kindly supplied by Dr. A. Björkman, Billeruds Aktiebolag, Säffle, Sweden).

The following humic acids were examined by high- and low-voltage electrophoresis (buffer pH range: 1·09–12·0):

(i) the preparation from site B, Horizon No. 12, Gilar peat (cf. Coulson *et al.*, 1959);
(ii) the preparation from the clay fraction;
(iii) the commercial humic-acid sample;
(iv) that from the Irish peat.

The behaviour of fifteen humic-acid samples from the different layers of the North Wales peat (Coulson *et al.*, 1959) was studied by paper electrophoresis (pH 7·4 buffer at 10V./cm.) and paper chromatography (using various organic solvents).

Paper-strip chromatography of humic acids using ascending organic solvents

The technique was similar to one previously reported (Coulson, 1958).

Paper: Whatman No. 4, 18 in. by 2 in. strips.

Solvents: Some fifty organic-solvent systems were tested (Khan, 1958).

Apparatus: Glass tubes 20 in. by 3 in. diameter were fitted with rubber stoppers bearing glass rods hooked at one end to carry filter-paper strips in a vertical position (up to three).

Procedure: The humic acid (0·1 mg. in 0·1 N NaOH [0·1 ml.]) was applied to the paper strip at a point 1½ in. from the lower end which dipped into 10–15 ml. of the solvent at the bottom of the glass tube. After running (front 9–12 in. from the start) the strip was air-dried and

then examined under both ordinary and ultra-violet light. The most promising solvents were tried by both descending and multiple ascending techniques. A hydrophobic complex is formed when humic acid is precipitated with cetyl pyridinium chloride (Davies *et al.*, 1957). Attempts were made to separate this in a similar fashion, using lipophilic solvents, but without success.

Paper electrophoresis

(*a*) *High voltage. Apparatus*: The apparatus was similar to that used by Hall *et al.* (1957), as modified by Lloyd and Syers (1959).

The paper was sandwiched horizontally between fairly thin polythene sheets (0·1 mm. thickness Telcothene sheet) held between the smooth surfaces of two heavy hollow copper blocks cooled by circulating tap water through internal copper baffles. The two ends of the paper dipped into the buffer solution contained in 'Perspex' electrode vessels. The distance between the platinum electrodes was 60 cm. and electrophoresis was at 33 V./cm.

(*b*) *Low voltage. Apparatus*: A horizontal type (Wieland and Fischer, 1948); the 'Perspex' tank fitted with carbon electrodes 25 cm. apart could hold three strips of paper 5 cm. wide. Electrophoresis was at 10 V./cm. and 18 V./cm.

Procedure for both types of electrophoresis

Paper: Whatman Nos. 1 and 3.

Buffers: (*a*) sodium acetate-HCl : pH 1·09, pH 3·09, pH 4·19, pH 5·2.
(*b*) phosphate-NaOH : pH 8·6, pH 9·0, pH 10·0.
(*c*) borate-KCl-NaOH : pH 8·6, pH 9·0, pH 10·0.
(*d*) citrate-phosphate-borate-barbiturate-NaOH: pH 11·0, pH 12·0 ((*a*)–(*d*): Vogel, 1953).
(*e*) barbiturate-acetate-H_2SO_4 : pH 8·6 (King and Wootton, 1956).

Method: Humic-acid solutions (1 mg./1 ml.; direct in buffer if pH $> 6{\cdot}00$, in 0·1 N NaOH if buffer pH $< 6{\cdot}00$) were applied with a loop of platinum to moistened paper in the tank. N-dinitrophenyl derivatives of glycine and ethanolamine (DNP-glycine and DNP-ethanolamine) were used as fast and zero markers respectively. The electrophoretograms were dried and photographed with visible and ultra-violet light.

Glass paper electrophoresis

Electrophoresis of humic-acid and lignin preparations was attempted on glass filter paper at 33 V./cm. as described by Lindgren (1958) using 0·05 N NaOH as the electrolyte. An imported product (supplied by W. & R. Balston) was used as a substitute for S. & S. Glasfaserpapier Nr. 6 used by Lindgren.

Colour-density curves

Curves were drawn from the electrophoretograms by an automatic double-beam densitometer ('Chromograph'. Joyce, Loebl & Co., Newcastle; 1958 model).

Ion-exchange synthetic resins, and other ion-exchangers (Calmon and Kressmann, 1957)

(*a*) *Synthetic resins.* The following ion-exchange resins were buffered (Vogel, 1953) and eluted:

'ZeoKarb' 225 at pH 4·8 (acetic acid—sodium acetate buffer).
'ZeoKarb' 226 at pH 6·4 (KH_2PO_4 and NaOH).
'Amberlite' CG 50 (200-mesh) at pH 6·4 and pH 7·0.
'De-Acidite' G at pH 6·4.
'Amberlite' CG 45 (200-mesh) at pH 6·4.

Humic-acid solution (1 ml. ≡ 10 mg.) was added to the top of a column (20 cm. by 1 cm.) after the buffer had been drained so that no surplus remained above the resin. The humic-acid solution was drawn into the column, a cotton wool pad placed in position and the column eluted with the buffer.

(*b*) *Cellulose ion-exchange absorbents* (Sober and Peterson, 1956).
NN Diethylaminoethyl (DEAE)—cellulose (Eastman Kodak Ltd.).
ECTEOLA—cellulose (Peterson and Sober, 1956).

(*c*) *Tube-testing technique* (Hirs *et al.*, 1953). For rapid testing of the potentialities of various ion-exchange materials for fractionating humic acid a method similar to that of Hirs *et al.* (1953) was adopted. The cellulose ion-exchanger (0·5 g.) was placed in a series of test-tubes and buffered at pH 5·0, 6·0, 6·5, 7·4, and 9·0 and the supernatant buffer solution poured off after low-speed centrifuging. Humic-acid solution (4 mg. in 2 ml. of appropriate buffer) was added to each tube and shaken. The humic acid could not be removed. (It had presumably precipitated, as with cetyl trimethyl ammonium bromide, Davies *et al.*, 1957.)

Attempts were made by this method to see whether humic acid could be displaced by sulphate from 'Amberlite' CG 50 (200-mesh) buffered at pH 6·0 and pH 7·0 using molarities of sodium sulphate: M/1, M/2, M/4, M/8, M/10, M/50, M/100, M/1000.

(*d*) *Ion-exchange papers* (*ascending paper chomatography*). Three types of ion-exchange papers (kindly supplied by Messrs. W. & R. Balston of Kent) were used with buffers of pH 6·4, 7·0, and 8·0:

(i) a cation-exchanger of the carboxymethyl type;
(ii) cellulose containing an amino-group;
(iii) phosphorylated cellulose containing approximately 8 per cent. P.

'Celite' 535 as an absorbent in columns (Hirs *et al.*, 1953; Lemieux *et al.*, 1956; Neish, 1949).

As a result of paper-chromatographic studies, *iso*propanol-water mixtures (6:4; 9:1; 15:1) were used with 'Celite' 535 (diatomaceous earth: Johns Manville) column. Humic-acid solution (10 mg. dissolved in pH 7·0 phosphate buffer) was absorbed on dry 'Celite' 535 (0·5 g.), layered on to the top of the column and eluted with the *iso*propanol-water mixture at 1 drop/20 sec. When 75 ml. were collected the column was allowed to run dry and after extrusion the residual layer on its surface and the very streaky layer below were cut out. These, and the eluate concentrated to 1 ml., were hydrolysed with 6 N HCl, the

hydrolysates were desalted electrolytically and then examined for amino-acids by two-dimensional paper chromatography (Coulson *et al.*, 1959).

Ouchterlony gel diffusion plates (Ouden, 1952)

By analogy with antibody-antigen analyses, gelatine-gel diffusion plates were set up. Fractions having different diffusion rates travel as separate bands which can be immobilized by a counter-diffusing precipitant. Gelatine was chosen as the medium rather than agar-agar or silica gel because the precipitant used (cetyl pyridinium chloride) is a general one for polyanions (Scott, 1955; Scott *et al.*, 1957).

An aqueous gelatine solution (1 per cent.) was poured into Petri dishes, as for bacterial culture (0·1 per cent. phenol was incorporated to prevent bacterial liquefaction). Small wells were cut out of the gel with a scalpel and various humic-acid solutions (pH 7·0) were placed in the outer wells with cetyl-pyridinium-chloride solution (2 per cent.) in the central well. The usefulness of the experiment was ultimately determined by the gelatine dissolving in the detergent.

Liesegang diffusion tubes (Hedges, 1932) were also tried. To gelatine solution (20 ml.) a 20 per cent. detergent solution (1 ml.) was added and a stab injection of humic acid was made using a platinum loop. The tube was kept in the dark and examined from time to time for ring formation.

Results

(i) *Paper chromatography using organic solvent-water mixtures*

Plate I shows the results of ascending paper chromatography (ultra-violet photography) for five of the better solvents. Yellowish green fluorescence was seen around the brown spots or streaks already visible in ordinary light; in general, fluorescent areas coincided with the spots or streaks seen on the paper after air-drying. Other systems giving results similar to the *iso*propanol/water (6/4) were tetrahydrofuran/water (9/1) and dioxane/water (9/1). These three systems seemed most promising. A fuller account is given elsewhere (Khan, 1958).

(ii) *Descending paper chromatography*

This proved less satisfactory than the ascending paper chromatography, since much more streaking occurred.

(iii) *Column chromatography*

The results obtained by eluting humic acids through a column of 'Celite' 535 with *iso*propanol/water (6/4, 9/1, and 15/1) showed considerable fluctuation; sometimes bands appeared, then later changed to streaks. *Iso*propanol/water (6/4 and 9/1) caused more streaking than (15/1). In several attempts with *iso*propanol/water (9/1) some five to seven bands were seen moving in the early stages (the first 5 cm.). In general, however, there appeared to be only three recognizable fractions:

(*a*) A residual fraction of humic material on the surface of the column.
(*b*) A dark band about 2 cm. from the top; this band became wavy with streaking of material for a short distance.

(*c*) A distinct yellow to yellowish brown band which persisted downwards and was collected as the eluate.

The amino acids present in (*a*), (*b*), and (*c*) are given in Table 1.

TABLE 1

Amino acids in the Humic-acid Fractions from 'Celite' Column

Amino acid	*Original humic acid*	*Celite residue* (*a*)	*Column streak* (*b*)	*Fraction eluate* (*c*)
Aspartic acid	Very strong	Strong	Weak	Trace
Glutamic acid	Very strong	Strong	Weak	Trace
Serine	Strong	Weak	Weak	Moderate
Glycine	Strong	Weak	Weak	Weak
Threonine	Strong	Weak	Trace	Trace
Alanine	Very strong	Moderate	Weak	Weak
Tyrosine	Weak	..	..	..
Proline	Weak	..	..	Trace
Valine+Methionine	Very strong	Weak	Weak	Weak
Phenylalanine	Moderate	..	..	Trace
Leucines	Very strong	Weak	Weak	Very strong

Aspartic acid and glutamic acid were particularly rich in the hydrolysate of the residual surface layer (*a*) and the leucines noticeably rich in the hydrolysate of eluate (*c*). The other amino acids found in the hydrolysate of the original peat humic acid were also in the hydrolysates of the three fractions (though tyrosine was not detected in any of them) and the hydrolysate of the streaky material (*b*) seemed to be the lowest in amino-acid content.

(iv) *Ion-exchange*

(*a*) *'Zeo-Karb' 225.* Elution of humic acid with pH 4·8 buffer down a column of 'Zeo-Karb' 225 buffered at pH 4·8 (the buffer in each case was acetic acid—sodium acetate) gave a continuous streak of humic material which passed out in the eluate without any apparent fractionation. The high levels of amino acids show that no significant removal of nitrogen had been achieved, unlike that reported for a similar resin by Drozdova (1955). The column was next eluted with 2 per cent. NaOH solution and this eluate collected separately. Each eluate was hydrolysed and developed as a two-dimensional paper chromatogram as before. Whereas the usual amino-acid pattern appeared in that of the first eluate, only traces were observed in the second. This method clearly gave no fractionation of the humic acids nor was there indication of removal of amino acids; cf. results obtained with detergents (Davies *et al.*, 1957).

(*b*) *'Zeo-Karb' 226 and 'Amberlite' CG 50 (200-mesh).* Elution of humic acids in columns of these materials (buffered at pH 6·4 by KH_2PO_4 and NaOH) resulted in the humic acids passing through as a single band which was especially sharp when 'Amberlite' CG 50 was used; no fractionation was achieved.

In a series of tube tests with similarly buffered sodium-sulphate solutions (M/1 to M/1000 with respect to Na_2SO_4) there was no evidence of displacement of the humic acid by sulphate.

(*c*) *Other ion-exchange materials.* 'Amberlite' CG 45 (200-mesh), De-Acidite G, the cellulose ion-exchangers DEAE-cellulose and ECTEOLA-cellulose, as well as ion-exchange papers of the carboxymethyl type, phosphorylated type, and the aminated type did not fractionate humic acid (Khan, 1958).

(v) *Gel diffusion*

Neither the Ouchterlony gelatine-gel diffusion plates nor the Liesegang tubes assisted the fractionation of humic acid.

(vi) *Paper electrophoresis*

(*a*) *High voltage* (Plates II and III and Table 2). Plate II shows the results of paper electrophoresis at high voltage and in various buffers

TABLE 2

Conditions of High-voltage Electrophoresis (60 cm. between electrodes)

Whatman Paper no.	*Buffer pH*	*Start*		*Finish*		*Time of run (min.)*
		Volts	*Milliamp.*	*Volts*	*Milliamp.*	
3	1·09	1,000	65	1,920	100	52
3	3·09	2,000	165	1,400	190	42
3	4·19	2,000	130	1,850	200	54
3	5·20	2,000	167	1,850	235	51
1	6·40	2,000	14	2,000	27	97
3	7·00	2,000	50	2,000	78	42
3	7·40	2,000	54	2,000	75	35
3	8·00	2,000	62	2,000	90	38
3	8·60	2,000	50	2,000	71	57
3	9·00	2,000	55	2,000	85	40
3	10·00	2,000	70	2,000	105	55
3	12·00	2,000	65	1,920	100	52

ranging from pH 1·09 to 12·00 for four humic acids from various sources. The key to the four designated in Plate II is:

C, Humic acid from clay fraction (Aber soil).

L, Commercial humic acid from certain bituminous deposits extracted by alkali (Light & Co.).

M, Humic acid from Irish peat extracted by alkali at high temperature under nitrogen (kindly supplied by Dr. D. Murphy, Dublin).

B_{12}, Humic acid extracted by neutral sodium pyrophosphate (Coulson *et al.*, 1959) from a peat sample of site B, Horizon 12, of the bog at Gilar.

The spots on both sides of the electrophoretograms are the fast and slow markers (the N-dinitrophenyl derivatives of glycine and ethanolamine respectively).

Electrophoresis was started at 33 V./cm. in all cases except for buffer

pH 1·09, where it was impracticable. Details of the conditions for electrophoresis are given in Table 2.

As Plate II shows, there was hardly any movement. With buffer pH 3·09 there was a slight streak for about 5 cm. With buffers ranging from pH 4·19 to 12·00 there was streaking for 10 cm.–20 cm., but there appeared to be a narrowing of the streaky band at about midway along the length of the streak, so that careful observation showed the presence of a faster component of high migration value under these conditions.

The transport of spots of humic acid, independent of any applied potential difference, was observed as a consequence of slow siphoning of the buffer.

Plate III shows the movements obtained after standing for ¾ hour in the high-voltage apparatus with pH 8·6 buffer and 12 hours in the low-voltage apparatus with pH 10 buffer. The distance was never more than 4 cm. in any case. Our glass-fibre paper, used as an alternative to ordinary paper, showed no fractionation of lignins or humic acids, unlike that of Lindgren (1958). This may have been due to some difference in the papers from that used by Lindgren.

(*b*) *Low voltage* (Plates III and IV and Table 3). Plate IV shows the results obtained by paper electrophoresis of humic acids (assigned the same letters as in Plate II) at low voltage (10 V./cm.). Additional humic-acid preparations were used: site B, Horizon 8 (B_8) and site A, Horizon 1 (A_1) from the Gilar peat (see Coulson *et al.*, 1959). It will be seen that a 'salting-out' effect sometimes occurred, e.g. with buffers of pH 10 and pH 12. The fast and slow markers were as in Plate II and were run in buffers of pH 7·0, 8·6, and 12·0. The conditions are detailed in Table 3.

TABLE 3

Conditions of Low-voltage Electrophoresis (25 cm. between electrodes)

Whatman Paper no.	*Buffer pH*	*Start*		*Finish*		*Time of run (hours)*
		Volts	*Milliamp.*	*Volts*	*Milliamp.*	
1	3·09	100	30	100	50	2
1	4·19	250	36	250	92	3
1	5·20	250	32	250	86	3
1	6·40	450	12	363	20	2
1	7·00	250	12	245	20	5
1	7·40	250	7	250	21	2
1	8·00	250	6	250	16	3
1	8·60	250	12	250	20	7
1	9·00	250	12	250	20	4
1	10·00	250	12	250	20	4
1	12·00	250	12	250	20	7

Electrophoresis was at 18 V./cm. in the exceptional case of pH 6·4 buffer. Electrophoresis at pH 3·09 did not result in the movement of

any humic material, there was slight streaking for a very short distance in buffers of pH 4·19 and 5·20 and signs of separation appeared when the buffer was pH 6·4. In buffers pH 7 to 12 a major component was mobile, and a small component did not move. The region between these two was occupied by a 'band' of streaky material. Some 'salting-

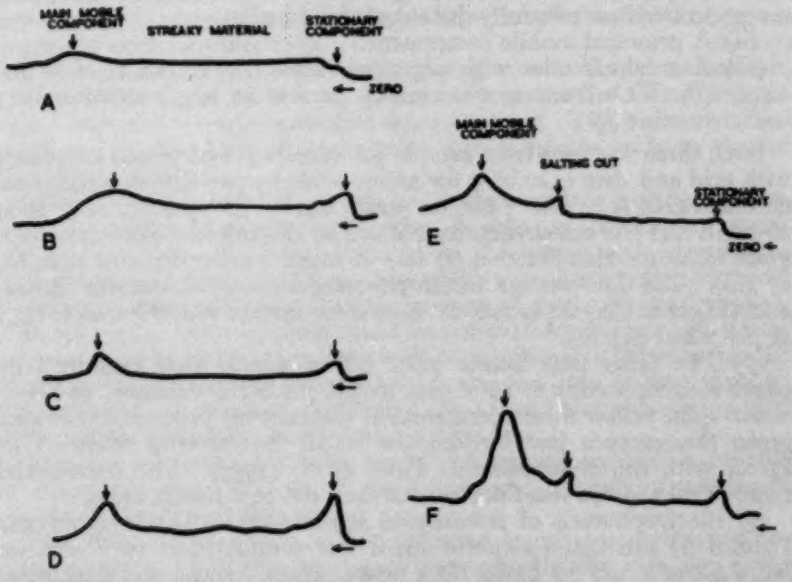

FIG. 1. Colour-density curves of humic acid electrophoretograms. A, B_8 at 10 V./cm. in pH 8·6 veronal buffer; B, L (under the same conditions (A)); C, B_8 at 10 V./cm. in pH 7·0 buffer; D, L (under the same conditions (C)); E, B_8 at 10 V./cm. in pH 12·0 buffer; F, L (under same conditions (E)).

out' appeared under these conditions of examination (possibly due to excessive evaporation at the centre).

The results may be summarized as follows:

(*a*) The patterns of the electrophoretograms were not different whether the humic acids were applied as a solution in 0·1 N NaOH when the buffer was pH below 6·4 or as one directly dissolved in the buffers at higher pH (see Plate IV: electrophoretogram in buffer pH 7·4).

(*b*) The best results were obtained at 10 V./cm. and gave less streaking than at 18 V./cm. and much less than at 33 V./cm.

(*c*) Electrophoretic movement was insufficiently great in buffers more acid than pH 4·19 at 33 V./cm. and pH 6·4 at 10 V./cm.

(*d*) Plate IV and Fig. 1 illustrate the 'salting-out effect' which sometimes occurred when electrophoresis was carried out at 10 V./cm. in buffers of pH 10 and pH 12.

(*e*) Fig. 1 shows colour-density curves for some of the electrophoretograms.

In buffers pH higher than 6·4 three main fractions were recognized:

(i) A small neutral fraction at the starting-point. Robinson, Martin, and Page (1951) report its presence, but Swaby (1958) pointed out that it was not noticeable. There seems to be less in some preparations than others, e.g. the sample of Irish peat was found to be almost entirely devoid of this fraction.
(ii) A principal mobile component.
(iii) A streaky fraction with migration values between those of (i) and (ii). This fraction was usually present in larger amounts than fraction (i).

Such three fractions from sample B8 were each hydrolysed separately with acid and then examined for amino acids by two-dimensional paper chromatography. The patterns were similar in quality, but their strength and the colour-density pattern of the original electrophoretogram indicated that fraction (i) was in much smaller amount than (ii) or (iii). The low-voltage electrophoretograms of commercial humic acid (Light & Co.) do appear to show some further minor bands (Fig. 1 at pH 7 and pH 12).

(*f*) The Gilar peat humic acids (all of which were examined by paper electrophoresis at 10 V./cm. in pH 7·4 buffer) showed, in ultraviolet ight, yellow fluorescent areas at the starting point and yellowish green fluorescence just beyond the major fast-moving front. This agrees with the observation of Pavel *et al.* (1953). The commercial humic acid showed less fluorescence than the peat humic acids.

(*g*) Electrophoresis of commercial lignin samples (Soda lignin and Indulin A) and lignin-sulphite liquor was conducted at 10 V./cm. on No. 1 paper in pH 7·4 buffer for 3 hours. Plate V shows the similarities with humic acid. The lignin-sulphite liquor showed more than one main component, but it contained other degradation products (as well as free amino-acids and free sugars).

Discussion

The elucidation of the chemical and physical nature of the mixture that constitutes humic acid cannot make rapid headway till means are devised to separate the acid into its fractions. Great difficulty has been encountered in past attempts to do this, and in future attempts more pains will have to be taken in applying modern methods. The present account of the study of humic acids by chromatography, electrophoresis, and diffusion is a contribution to this end.

Some solvent systems in ascending paper chromatography produced a little separation. Many others either failed to move the acids at all or produced only a streaky separation; multiple development and descending techniques were no better. The complex with cetyl pyridinium chloride (Davies *et al.*, 1957) did not fractionate during paper chromatography. The ion-exchange resins and the cellulose ion-exchange materials (as well as ion-exchange papers) failed to give any fractionation. Hopes that fractionation of the humic acid would be achieved by column chromatography were not fulfilled though three tentative fractions

were examined. These did differ in some details, e.g. in amino-acid content.

Examination of the humic acids by paper electrophoresis showed a principal component of high migration value, a stationary component present in small concentration, and other material of varied migration values. Robinson *et al.* (1951) have reported similarly in studies on organic colloids from Brookston clay as have Scheffer and his colleagues (1955) on those of other soils.

Electrophoresis at low potential drop gave the best fractionation, judged from visible movement of the material, but chemical analysis of the fractions did not consolidate this judgement. There was a marked similarity in the electrophoretic behaviour of humic acids to that of commercial lignins.

These physico-chemical studies do, perhaps, throw a little light on the nature of this fraction of soil humus. In many of the solvent systems which were tried only minor portions of the humic acids moved, the bulk remained behind. In those cases where several spots formed, these spots again constituted only a minor portion of the humic acid applied. The substances forming them could be removed by dialysis and it may be concluded from this that they were of significantly lower molecular size than the bulk of the material which was too large to pass through the cellophane membrane. Bremner (1955) found that these accounted for less than 1 per cent. of humic-acid nitrogen.

The best solvents were those containing organic substances capable of dissolving some at least of the humic acid, namely: *iso*propanol, tetrahydrofuran, and dioxane.

The fractionation of humic acid achieved in column partition chromatography using 'Celite 535' and *iso*propanol/water was not easily reproducible and at best obtained only to a depth of 4–5 cm. before streaking ensued. The instability of the bands points to the need for careful control of conditions during development and may be inherent in the character of the humic acids themselves. Dawson (1956) is indeed pessimistic about the possibilities of fractionation of humic acids by partition.

Paper electrophoresis divides the acid into three distinct groups. The first component may be stationary because of adsorption on the paper or because it is neutral. The fast-moving component may not be a single substance but a group of closely related substances, as is thought with lignin (Scheffer *et al.*, 1955; Schubert and Nord, 1957). The material producing a streak may do so either by continuous adsorption on the paper of the fast-moving component or it may be a multitude of substances of gradually increasing mobility.

That there was no banding, when humic acids diffused in gelatine, would seem to support Stevenson, Van Winkle, and Martin (1953) whose measurements of sedimentation-velocity by ultra-centrifugation and of diffusion constant indicated that the humic acids were polydisperse with respect to particle size.

These present investigations indicate the complex nature of the humic acids, but the chromatography and electrophoresis do give some

hope of fractionation. The average molecular weight of about 53,000 suggested by Stevenson and others (1953) and Wright *et al.* (1958) (although Welte, 1955, considers the molecular weight to be about 1,000) points to the need for the detailed application of newer methods now in use for the fractionation of high-molecular-weight materials.

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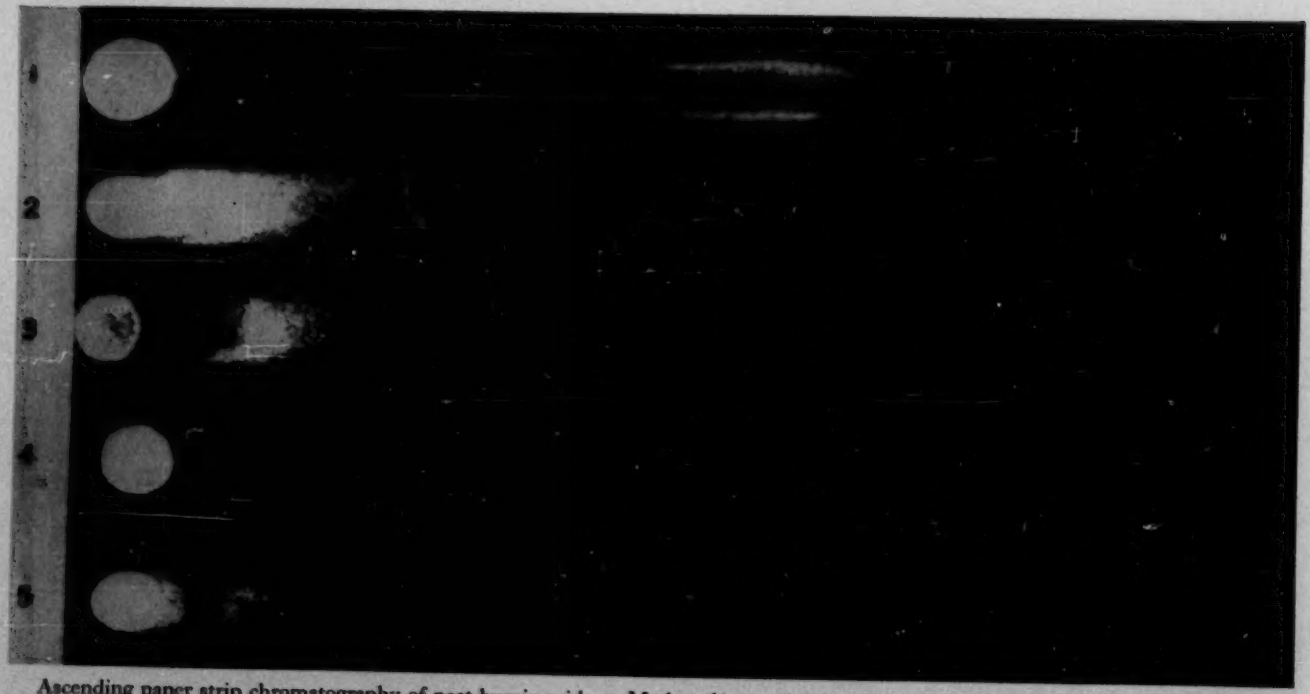
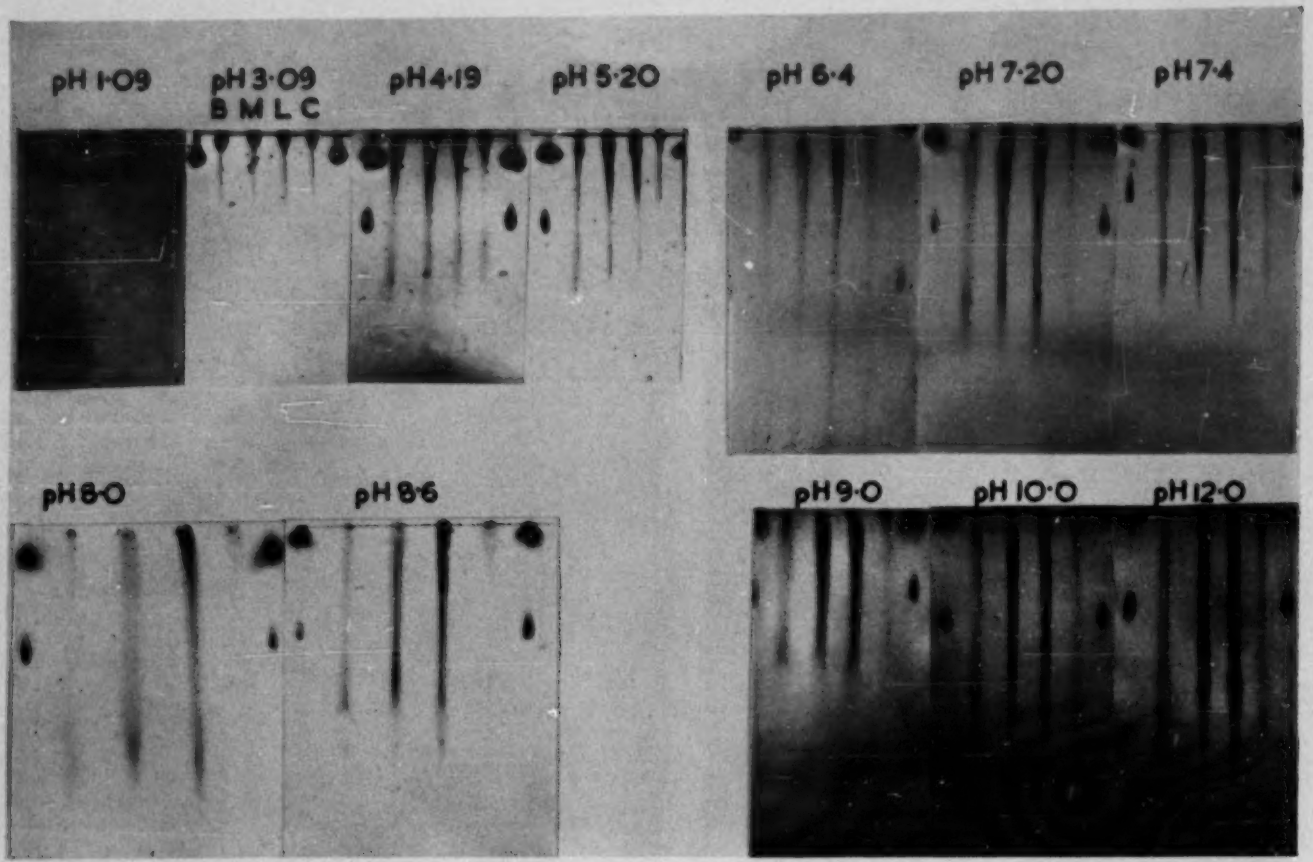
REFERENCES

Bremner, J. M. 1955. J. Agric. Sci. **46**, 247.
—— and Arnold, P. 1952. Unpublished.
—— and Lees, H. 1949. J. Agric. Sci. **39**, 274.
Calmon, C., and Kressman, T. R. E. 1957. Ion Exchangers in Organic and Biochemistry. New York: Academic Press Inc.
Coulson, C. B. 1958. J. Sci. Fd. Agric. **9**, 281.
Davies, R. I., Coulson, C. B., and Luna, C. 1957. Chem. and Ind., 1544.
Dawson, J. E. 1956. Adv. Agronomy, **8**, 377.
Drozdova, T. V. 1955. Pochvovedenie No. 1, 83.
Eller, W. 1923. Ann. Chem. **431**, 133.
—— Herdieckerоff, E., and Saenger, H. 1923. Ibid. **431**, 177.
—— and Koch, K. 1920. Ber. Deutsch. Chem. Ges. **53**, 1469.
Forsyth, W. G. C. 1947. Biochem. J. **41**, 176; see also 1950, **46**, 141.
Hall, D. A., Lloyd, P. R., Happey, F., Horton, W. G., and Naylor, A. 1957. Nature, **179**, 1078.
Hedges, E. S. 1932. Liesegang Rings and Other Periodic Structures. London: Chapman & Hall. See also King, A. Inorganic Preparations 1936, p. 16. London: Murby.
Hirs, C. W. H., Moore, S., and Stein, W. H. 1953. J. Biol. Chem. **200**, 493.
Hock, A. 1937. Bodenk. PflErnähr. **5**, 1.
Khan, E. J. A. 1958. M.Sc. Thesis, Univ. Wales.
King, E. J., and Wootton, I. D. P. 1956. Microanalysis in Medical Biochemistry. 3rd ed., p. 122. London: Churchill.
Kononova, M. M., Belchikova, N. P., and Nikiforov, V. K. 1958. Pochvovedenie No. 3, 83.
Laatsch, W. 1944. Dynamik der deutschen Acker- und Waldböden. 2nd ed., p. 75. Dresden and Leipzig: Steinkopf.
Lemieux, R. V., Bishop, C. T., and Pelletier, G. E. 1956. Canad. J. Chem. **34**, 1365.
Lindgren, B. O. 1958. Acta Chem. Scand. **12**, 447.
Lloyd, P. F., and Syers, K. 1959. To be published.
Neish, A. C. 1949. Canad. J. Res. **27B**, 6.
Ostwald, W., and Steiner, A. 1925. Kolloidchem. Beihefte **21**, 97. Cf. Waksman, S. A. 1936. Humus, p. 311. London: Bailliere, Tindall & Cox.
Ouden, J. 1952. Methods in Medical Research, **5**, 335. New York: Year Book Publ. Inc.
Pavel, L. 1958. Private communication.
—— Koloušek, J., and Šmatlák, V. 1953. Ann. Acad. tchécosl. Agric. **26A**, 155.
Peterson, E. A., and Sober, H. A. 1956. J. Amer. Chem. Soc. **78**, 751.



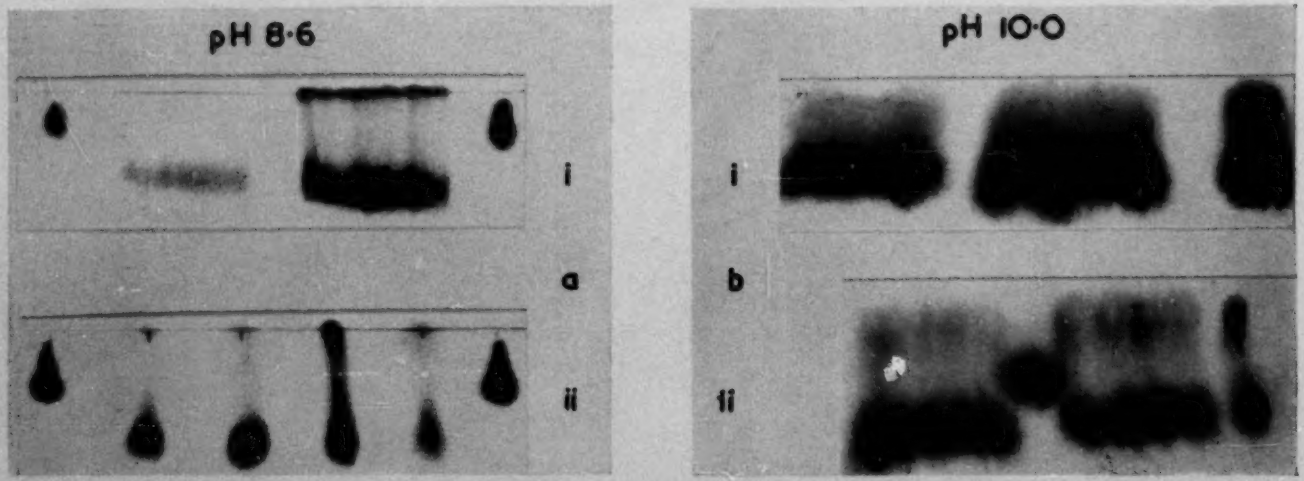
Ascending paper strip chromatography of peat humic acid. 1, Methanol/water (1/1); 2, *n*-Butanol/ethanol/water (1/1/1); 3, Ethyl acetate/pyridine/water (2/1/2); 4, Ethanol/0·88 ammonia/water (16/1/1); 5, *Iso*propanol/water (3/2).

C. B. COULSON, R. I. DAVIES, *and* E. J. A. KHAN—PLATE I



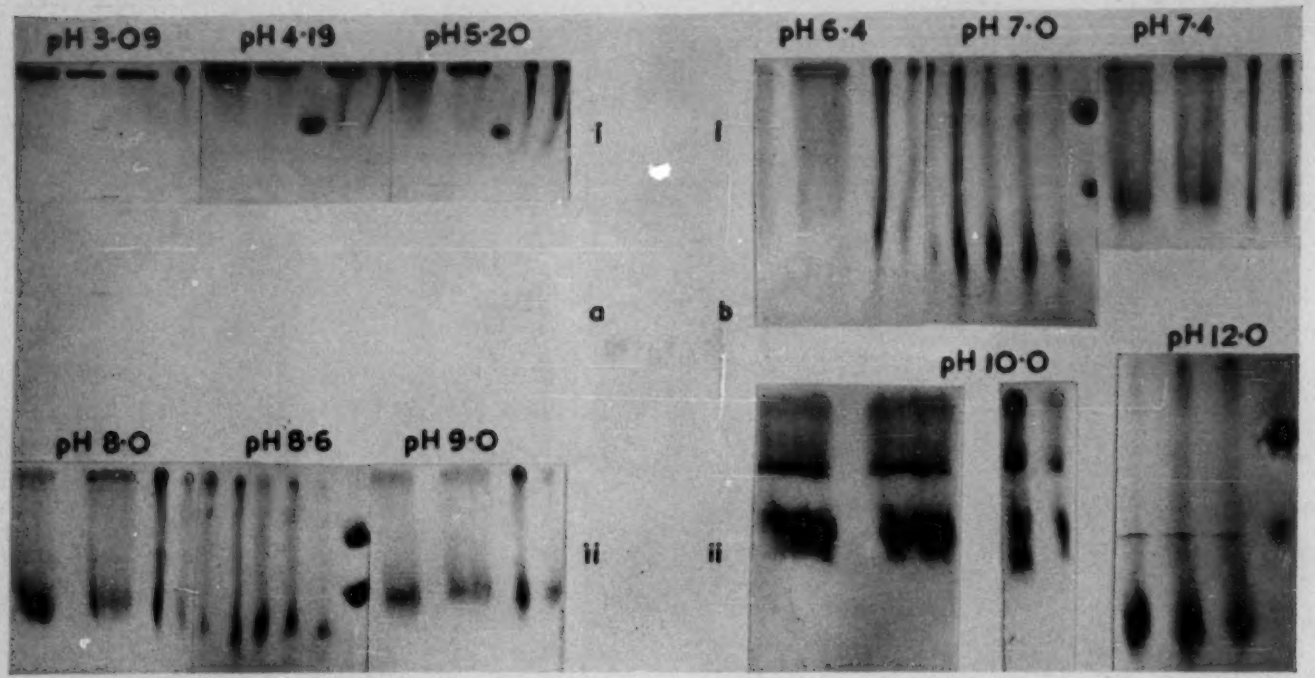
Electrophoresis at high voltage and various pH. The symbols B (B_{12}), M, L, C are explained in the text. They are in that order in each electrophoretogram. DNP-ethanolamine is the slow marker and DNP-glycine the fast marker (on either side of the four humic acids).

C. B. COULSON, R. I. DAVIES, *and* E. J. A. KHAN—PLATE II



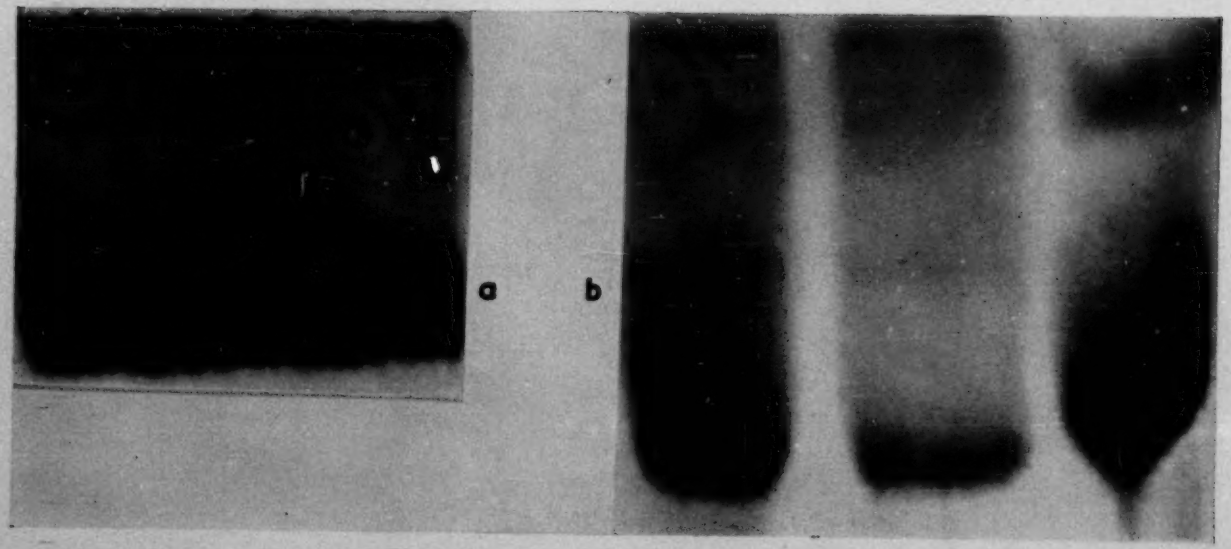
Movement of humic acids by buffer movement alone. (*a*) In high-voltage apparatus at pH 8·6 (i) B and L, (ii), B, M, L, C (together with markers as before). (*b*) In low-voltage apparatus at pH 10·0: (i) A_1, B_a, L, (ii) A_1, DNP markers, B_a, L.

C. B. COULSON, R. I. DAVIES, *and* E. J. A. KHAN—PLATE III



Electrophoresis at low voltage carried out at different pH. The peats are as follows: (*a*) (i) all A_1, B_8, L, B_8: in that order. (ii) A_1, B_8, L, B_8; C, L, M, B, B, DNP derivatives; A_1, B_8, L, B_8. (*b*) (i) A_1, B_8 (in buffer), A_1, B_8 (in buffer), A_1, B_8 (in 0·1 N NaOH); C, L, M, B_8, DNP derivatives; A_1, B_8 (in buffer); L, B_8 (in 0·1 N NaOH); (ii) A_1, B_8, L, B_8; M, B_8, B_{12}, DNP derivatives.

C. B. COULSON, R. I. DAVIES, *and* E. J. A. KHAN—PLATE IV



Electrophoresis at 10 V./cm. in pH 7·4 buffer.
a. Peat humic acid. *b*. 'Soda lignin'; 'Indulin A'; and 'Sulphite liquor'.

C. B. COULSON, R. I. DAVIES, *and* E. J. A. KHAN—PLATE V

ROBINSON, D. O., MARTIN, W. P., and PAGE, J. B. 1951. Ohio Expt. Sta. Bull. 705, 18 (69th Ann. Rep.).
RUSSELL, E. J., and RUSSELL, E. W. 1952. Soil Conditions and Plant Growth. 8th ed., p. 255. London: Longmans, Green.
SCHEFFER, F., ZIECHMANN, W., and SCHLUTER, H. 1955. Z'PflErnähr. Dung. **70**, 260. See also FLAIG, W., SCHEFFER, F., and KLAMROTH, B., ibid., p. 33.
SCHUBERT, W. J., and NORD, F. F. 1957. Adv. Enzymol. **18**, 356.
SCOTT, J. E. 1955. Chem. and Ind., 168.
—— GARDELL, S., and NILSSON, I. M. 1957. Biochem. J. **67**, 7P.
STEVENSON, F. J., MARKS, J. D., VARNER, J. E., and MARTIN, W. P. 1952. Proc. Soil Sci. Soc. Amer. **16**, 69.
—— VAN WINKLE, Q., and MARTIN, W. P. 1953. Ibid. **17**, 31.
SWABY, R. J. 1958. Lecture in University College of North Wales, Bangor. See also 8th, 9th, and 10th Ann. Reps. C.S.I.R.O., Australia, 1956–8.
VOGEL, A. I. 1953. A Text Book of Quantitative Inorganic Analysis, p. 868. 2nd ed. London: Longmans, Green.
WELTE, E. 1955. Angew. Chem. **67**, 153.
WIELAND, T., and FISCHER, E. 1948. Naturwiss. **35**, 29.
WRIGHT, J. R., SCHNITZER, M., and LEVICK, R. 1958. Canad. J. Soil Sci. **38**, 14.

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INCREASES IN THE CARBON AND NITROGEN CONTENTS OF TROPICAL SOILS UNDER NATURAL FALLOWS

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Summary

The rate of increase of humus carbon in soils rested under natural fallows has been calculated, assuming that the rate of decomposition of the humus carbon is proportional to the amount present, and that the rate of addition, by humification of litter and roots, remains constant. The rate of decomposition has been derived from a knowledge of the maximum humus level the soil attains under the fallow vegetation, and the rate of addition has been estimated from data on litter production. The rate of increase of nitrogen has also been calculated assuming that the C/N ratio in the soil remains constant. Under the native practice of shifting cultivation in forest the alternation of cropping and fallowing leads to relatively small fluctuations in soil humus at about 75 per cent. of the maximum level. The rates of increase of soil nitrogen at this level are between 20 and 50 lb. per acre per annum in forest and 4 and 10 lb. per acre per annum in savannah. Rates at other levels for which the assumptions made are valid may readily be calculated from the data presented. It is shown that provided vegetation re-establishes itself rapidly a crop:fallow ratio of about 1:3 should maintain the humus level in forest soils at the 75 per cent. of equilibrium level, a result which accords well with experience.

Introduction

ALTHOUGH restoration of soil organic matter is thought to be an important function of the widely practised system of natural fallows in the tropics, very little is known about how quickly and to what extent this is achieved. A search of the literature has failed to reveal any satisfactory measurements of the changes that occur in the soil under such fallows. There are a limited number of reports of the decline in organic matter that occurs during the cultivation period, but this is not particularly helpful unless it can be assumed that the fallow period in practice is just sufficient to make good this loss. In fact, the length of the fallow period is determined by a variety of factors in addition to soil fertility, particularly availability of land and the time required for the natural vegetation to eliminate weeds. An experiment has now been established in Ghana which should in time provide definite data on the rate of restoration of organic matter under various conditions. In the meantime, it is necessary to use a more theoretical approach to obtain an idea of the magnitude of the changes and the rate at which they occur. While this is in some ways less satisfactory than direct measurement it enables comparison to be made between the widely differing conditions of forest and savannah areas, and between tropical and temperate zones, and it also provides a basis for comparison with field observations and records. The aim of the present paper is therefore to deduce from published data what the changes of soil organic matter under natural

bush fallows are likely to be, assuming that the gains and losses of soil organic matter in such conditions conform to accepted theory.

Method

Changes in the amount of humus carbon in the soil are the result of differences between additions and losses. The addition and loss processes are illustrated diagrammatically in Fig. 1. It is seen that there are

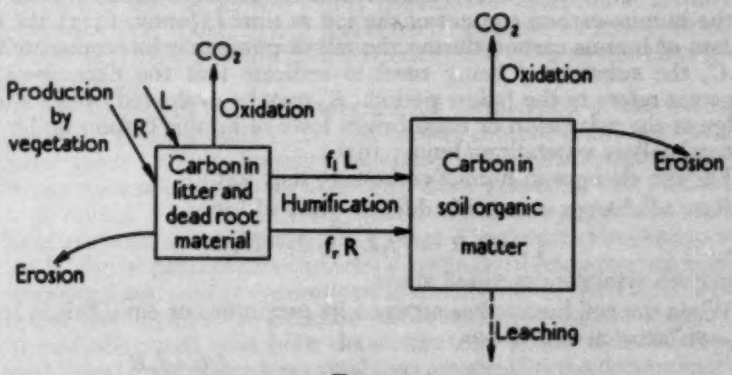

FIG. 1

essentially two systems to be considered; that of the litter and dead root material, including root exudates, shown to the left of the diagram, and that of the humified material shown to the right. It is the changes of humus* carbon which are of greatest interest to the agriculturist, and with which the present paper is primarily concerned.

Additions of humus

To determine the rate of addition of humus carbon the gains of carbon by the soil have to be estimated as fractions of fresh production of organic material. The quantities of litter and root material produced by different types of vegetation are therefore required. For litter production figures are available; for root material production figures have to be estimated from data on, for example, shoot to root ratio. Further the fractions of these materials lost prior to incorporation with soil humus must be known. While these may vary locally differences in the amounts of vegetation produced in different ecological zones are sufficiently great to outweigh local differences, and it is therefore possible to discover the general differences likely to occur between, for example, tropical forest and savannah zones and tropical and temperate regions.

If the amount of litter produced in unit time is L, and the amount of dead root material, including root exudates, added to the soil in unit time is R, then the addition to humus carbon in unit time is $f_1 L + f_2 R$,

* The term 'humus' is used to signify that recognizable plant remains are excluded from the soil organic matter considered in this paper. It does not refer to any chemically separable fraction of the soil organic matter.

where f_l and f_r are the fractions of the fresh litter and root material respectively added to soil humus, the remainder of the production being lost by oxidation, and perhaps also by leaching and erosion.

Losses of humus

By analogy with the cropping phase of the crop-fallow cycle, when the rate of loss of humus carbon is represented by the equation $-dC/dt = K_c C$, where K_c is the soil-humus decomposition constant and C the humus-carbon content of the soil at time t (Jenny, 1933), the rate of loss of humus carbon during the fallow phase may be represented by $K_f C$, the subscript f being used to indicate that the decomposition constant refers to the fallow period. K_f may be evaluated from a knowledge of the maximum or equilibrium level of humus carbon under the natural-fallow vegetation (Jenny, 1950).

For the changes in humus carbon we may write

Rate of change = rate of addition − rate of loss,

i.e. $$dC/dt = (f_l L + f_r R) - K_f C \qquad (1)$$

using the symbols described above.

When the soil humus has attained its maximum or equilibrium level, C_E, $dC/dt = 0$, and hence

$$K_f C_E = f_l L + f_r R \quad \text{and} \quad K_f = \frac{f_l L + f_r R}{C_E}. \qquad (2)$$

Data for soils in the virgin condition provide values for C_E, and so if the rate of addition of humus carbon is known the decomposition constant can be calculated.

Assumptions

In applying equation (1) the following assumptions are made:

(*a*) that there is a continuous addition of humus carbon to the soil;
(*b*) that this is added at a constant rate, i.e. that $(f_l L + f_r R)$ is independent of C;
(*c*) that the rate of humus decomposition is proportional to the amount present throughout the range of soil-humus contents considered.

In tropical rain forest (*a*) will be very nearly true, though some variation will occur during the year in the moist semi-deciduous forests which have a definite dry season. In savannah areas of pronounced dry season and in temperate areas it is definitely not true, litter fall and plant growth having a fixed seasonal pattern. But provided only periods considerably greater than one year are considered, and one year is taken as the unit of time, then little error is introduced even when the equation is applied to savannah and temperate regions.

(*b*) The rate of addition of humus carbon to the soil will not in general depend on the carbon content of the soil unless low organic-matter contents seriously reduce soil fertility and hence vegetation growth. By considering only soils containing more than 50 per cent. of their equilibrium content of humus carbon, as will be done in the

present treatment, the assumption that $f_l L$ and $f_r R$ are independent of C is justified.

(*c*) This is hardly an assumption, since many authors have now shown that, except at low levels of humus carbon, the rate of loss of carbon during cultivation is proportional to the carbon content of the soil (see, for example, the data discussed by Jenny, 1941; Hénin and Dupuis, 1945; and for recent data from the tropics, Birch, 1958). At low levels of humus the fact that a significant proportion of the humus carbon may be almost totally resistant to oxidation could introduce errors. The equation will therefore be applied, as stated already, only to soils containing more than 50 per cent. of their equilibrium level of humus carbon.

It might be argued that the experimental justification of the relationship between decomposition rate and carbon content refers only to the cropping phase. This is largely true, though Birch's laboratory studies of humus decomposition were done with both grassland and cultivated soils. If humus fractions differing widely in the rate at which they are oxidized are built up under the fallow, then the simple relationship will not hold. But at present no satisfactory methods of fractionating humus into more and less readily decomposable fractions have been established, nor have any significant chemical differences in organic matter in fallow and cultivated soils been demonstrated. Until such differences are established it would seem reasonable to assume that the decomposition of humus under the fallow is directly proportional to the amount present, as it is when the soil is cultivated.

Jenny and his collaborators (Jenny *et al.*, 1949; Jenny, 1950), who first developed this approach, calculated a decomposition constant for the soil carbon as a whole, including in the soil carbon the litter on the surface and freshly added material such as root slough and exudate in the soil. This constant is much greater than the decomposition constant for humus carbon alone, since the fresh organic matter is oxidized very much more readily than the carbon in humified material. These writers, in fact, calculated a decomposition constant for the litter layer of 40–60 per cent.* compared with an overall soil-carbon decomposition constant of 1–3 per cent. The advantage of determining the decomposition constant for the humus carbon alone is that while humus fractions differing slightly in the rate at which they decompose may be included within a single decomposition constant, litter and humus differing in rate of decomposition by a factor of 50 are separated. Assumption (*c*) is certainly not true if C is taken to include litter as well as humus carbon,

* Jenny *et al.* calculated the litter decomposition constant from the equation $A = K(F_E + A)$, where A is the rate of addition of litter in lb. per acre per annum, and F_E is the equilibrium level of litter carbon on the forest floor.

For tropical rain-forest conditions in which litter fall is fairly continuous, the appropriate equation, equalizing gains and losses over a short time δt, is however: $A\,\delta t = K\,\delta t\,(F_E + A\,\delta t)$ not $A\,\delta t = K\,\delta t\,(F_E + A)$ or $A = KF_E$ not $A = K(F_E + A)$. This leads to a decomposition constant for litter of 170 per cent. per annum (3·25 per cent. per week) in the per-humid tropical forest of Columbia; and emphasizes even more strikingly the difference between the rate of decomposition of litter and of humus in the tropical forest.

since the rate of decomposition will vary greatly according to the proportions of litter and humus carbon in the total. Another advantage of considering the humus carbon alone is that direct comparison may be made between decomposition constants for the fallow phase and decomposition constants for the cropping phase, i.e. of K_f and K_c.

The difficulty in limiting the decomposition constant to humus carbon is that it necessitates making an estimate of the proportions of fresh organic material that become embodied with soil humus.

Evaluation of the Decomposition Constant

To evaluate the decomposition constant, K_f, for any particular soil using equation (2), the equilibrium or virgin carbon content for the soil in the given environment must be known, as well as the annual productions of litter and dead root material L and R, by the vegetation, and the fractions of these incorporated with the soil-humus carbon, f_l and f_r.

1. *The equilibrium humus-carbon content of the soil profile, C_E*

Few determinations of the carbon content of soil profiles from virgin or very old secondary tropical forests have been published, most data referring to profiles that are not in the equilibrium state. Nevertheless, by confining attention to free-draining upland soils where the predominant clay mineral is kaolinitic, the available data indicate that the variation of the equilibrium carbon contents within any one ecological zone are relatively small. It is therefore considered that the figures for highland and lowland tropical forest given in Table 1 are probably widely typical of upper slope soils in these areas.* Data for forest profiles recorded in Table 1 have been recalculated from the original percentage composition data, where necessary, to give total weights of carbon to 12 in., assuming that the mass of 1 acre-12 in. of dry soil is 4×10^6 lb. Where soil analyses have been reported to more than 12 in. it has been assumed that the horizon containing the 12-in. depth is uniform. All data have been calculated to 12 in. because it is restoration of organic matter in the surface horizons that is agriculturally important, and in order that comparison may be made with decomposition constants for the cropping period, all of which are calculated for surface soil only. Actual soil densities may differ somewhat from the value used here (cf. Jenny's data for the Columbian high-organic-matter soils (Jenny, 1950) although determinations made by the authors on typical forest and savannah latosols in Ghana give figures very closely in agreement with the figure used. For soils of very different density the results may be considered to apply to the top 4×10^6 lb. of soil on 1 acre, rather than to one acre-foot.

Carbon data for long-uncultivated savannah soils are even scarcer

* While the majority of the free-draining soils developed over the great continental land masses under tropical forest and moist savannah are kaolinitic, there are soils in similar environments to those considered here, with different clay mineral composition, for instance soils influenced by volcanic ash, containing allophane. These may have very much higher carbon contents.

TABLE I

Soil-Humus Decomposition Constants and Corresponding Soil-Nitrogen Increments at 75 per cent. of Equilibrium

Area	Rainfall (in. p.a.)	Elevation (ft.)	L (lb./acre/annum)	C_E (lb./acre)	Max. K_1 (%)	Min. K_1 (%)	Annual soil-N increment at 75% C_E (lb./acre) Max.	Min.	Authority
Tropical-forest zone—Lowland									
Columbia (i)	330	100	3,500	352,000	0·51	0·20	27	11	Jenny, 1950
Ghana	60–80	0–1,500	4,800	97,000	2·47	1·00	50	20	Endredy and Montgomery, 1954
India	N.S.Q.	>400	4,800	45,600	5·45	2·18	55	22	Santyanarayana *et al.*, 1946
Belgian Congo	72	1,500	5,500	53,800	5·15	2·04	53	21	Germain and Evrard, 1956
Indonesia (i)	*c.* 120	1,500	4,800	66,000	3·64	1·46	50	20	Hardon, 1936
Mean (excluding Columbia)				65,600	4·18	1·67	52	21	
Tropical-forest zone—Highland									
Columbia (ii)	110	5,000	4,550	360,000	0·63	0·25	41	16	Jenny, 1950
Indonesia (ii)	*c.* 100	4,000	4,800	310,000	0·77	0·31	40	16	Hardon, 1936
Madagascar	*c.* 80	5·500	4,800	313,000	0·80	0·31	35	14	Pernet, 1953
Mean				321,000	0·73	0·29	39	15	
Tropical-savannah zone			R						
Humid	*c.* 50	<2,000	1,300	50,000	1·33	0·53	14	5	..
Sub-humid	*c.* 35	<2,000	400	15,000	1·22	0·49	5	2	..
Temperate zone			L						
Oak forest	30	5,000	680	80,000	0·43	0·17	4	2	Jenny, 1950
Pine forest	30	5,000	1,500	78,500	0·95	0·39	9	4	Jenny, 1950
Prairie	34	1,000	1,290	122,000	0·44	0·17	11	5	Rost and Alway, 1921

than for forest areas. Probable limiting values, rather than actual values, are therefore used in Table 1, the upper limit being taken as 50,000 lb. of carbon per acre for the humid savannah zone and the lower limit as 15,000 lb. per acre for the drier savannah areas. This is the range found in Ghana between rainfall limits of 60 and 39 in. per annum and corresponds closely to the carbon contents of the Nachingwea red loam and the Mtanana sandy loam described by Muir, Anderson, and Stephen (1957) from humid and sub-humid areas of Tanganyika.

For the sake of comparison with temperate areas, Jenny's (1950) data for Californian oak and pine forest have also been included, together with data for tall-grass prairie in Minnesota (Rost and Alway, 1921).

2. *The litter carbon, L*

Jenny (1950) and Laudelout and Meyer (1954) have determined the total annual litter fall under tropical rain forests. The values they report for 'equilibrium' forest show a range from 3,500 lb. of carbon per acre to 5,600 lb. per acre, with a mean value of almost exactly 4,800 lb. per acre per annum. It may be noted, however, that the two values given by Laudelout and Meyer for the early stages of the forest succession indicate that litter fall is then rather higher than under climax forest (*c.* 7,000 lb. per acre of carbon).

For the savannah areas the annual burn of the vegetation reduces the contribution of grass and tree litter to the humus carbon to a value that is low compared with the contribution of the roots, and it will be assumed to be zero.

Jenny (1950) gives values for oak and pine forests, and the average of the range of values he quotes for tall-grass prairie (Jenny, 1941) has served as a basis for calculation of temperate-zone constants.

3. *The root carbon, R*

The root-carbon addition cannot be directly measured. Bartholomew *et al.* (1953) at Yangambi, Belgian Congo, determined the total weight of roots under forest fallows of up to 17 years of age, and found that the greatest rate of increase occurred in the first 5 years of the fallow, when an average of about 1,500 lb. per acre per annum of carbon was added to live roots.* Thereafter the rate of increase of live root was almost negligible, presumably due to the fact that the amount of decay was equal to the amount of new growth. Considerable root decay probably occurred during the initial growth period also. The total carbon entering the soil at equilibrium might therefore be as much as twice the carbon added to the live roots in the early stages of development, a total of about 3,000 lb. of carbon per acre per annum. This is equal to slightly less than half the value for the carbon in the annual litter fall in newly regenerated forest at Yangambi. Jenny (1950) suggested that R might range from $0{\cdot}5\ L$ to $2{\cdot}0\ L$. From the data quoted

* It has been necessary to assume here and elsewhere that the carbon content of root material is 50 per cent. of the dry matter.

here the mean value for the forest areas would seem more likely to approximate to 0·5 L, and this value will be used in the present paper.

No satisfactory data for the rate of production of root carbon under natural fallows in the savannah zone are available. An estimate may be formed by combining values for the growth of aerial parts with an estimate of the ratio of production of shoots:roots. Numerous studies on this ratio for temperate climate grasses have been reviewed by Troughton (1957), including in particular a study by Weaver and Zink (1946) of American prairie grasses similar in habit to those of humid African savannahs. When growing under favourable conditions, temperate-climate grasses have a shoot:root production ratio of between 5 and 2 to 1. A value of 3:1 will be taken as an average for savannah conditions. Under humid conditions in Ghana (60 in. per annum), Nye (1958) obtained a figure of 8,000 lb. per acre for the annual production of aerial parts in old stabilized savannah. For drier conditions, the figure of 2,200 lb. per acre recorded by Weinmann (1948) under 35 in. per annum in Southern Rhodesia may be quoted. The estimates of annual root-material additions R are therefore 1,300 lb. of carbon per acre for the humid savannah and 400 lb. per acre for the sub-humid savannah, figures which will be taken to correspond to 50,000 and 15,000 lb. of carbon in the top 12 in. of soil respectively. Since over 90 per cent. of the roots are in the top 12 in. it is unnecessary to modify the value of R when considering the 0–12 in. layer, rather than the whole profile.

4. *The fractions, f_l and f_r, of litter and root material incorporated with the soil humus*

The fractions of litter and root material which become incorporated with the soil humus will vary according to the precise environmental conditions prevailing in any particular soil, and with the composition of the organic material. Thus the actual values of f_l and f_r will depend on the carbon/nitrogen ratio of the litter and root material and of the soil organic matter. Normally the greater the quantity of nitrogen in the litter and root material, and the greater the quantity of nitrogen fixed per unit of carbon oxidized in the soil, the greater will be f_l and f_r. It is probable that f_l and f_r will have different values at different stages during the fallow; for instance, the oxidation of litter is probably greater when the fallow is poorly established and the soil more exposed than at later stages. The quantity of litter carbon incorporated with the soil may also be greatly reduced by erosion of the litter layer. Highly acid soils or soils liable to waterlogging are likely to have high values of f_l and f_r, whereas in soils in which bacterial activity is more pronounced the loss of carbon through oxidation will probably be much greater. Variations in the activity of soil fauna may also have an important effect, the proportion of oxidation to humification varying considerably according to whether decomposition occurs on the soil surface or in the soil, after incorporation by a burrowing animal. Fungi may be so efficient that only 50 per cent. of the carbon they consume is oxidized (Russell, 1950), but we do not know that there is not further oxidation

before incorporation with soil humus occurs. In fact it almost certainly does.

The procedure which will therefore be adopted will be to calculate K_f for maximum values of f_l and f_r of $\frac{1}{2}$ and $\frac{1}{2}$ respectively, and minimum values of $\frac{1}{5}$ and $\frac{1}{5}$ respectively, which should cover the probable range of variation of K_f. Using these values for f_l and f_r, and assuming for the forest that $R = 0{\cdot}5\,L$, and for savannah $R = 0{\cdot}33\,L$, the formula becomes:

$$\text{Forest zone, max. } K_f = L/2C_E \text{ and min. } K_f = L/5C_E,$$

$$\text{Savannah zone, max. } K_f = L/6C_E \text{ and min. } K_f = L/15C_E.$$

The Values of the Decomposition Constants

Values for decomposition constants are collected in Table 1. It is seen that for tropical rain forest there is a large difference between areas at different altitudes. This corresponds to the wide variation between carbon contents of the soil profiles in highland and lowland forest, litter-fall values being relatively constant. In the lowland forest, however, with mean soil temperatures of 22°–28° C., the variation in K_f does not exceed a factor of about 2, except for the low-altitude Columbian (Calima) profile, which is exceptionally high in organic matter. This profile was developed under exceedingly high rainfall, 330 in. per annum, had a very low calcium saturation, and the unusually high C/N ratio of 20:1 in the surface horizon, suggesting development of a more resistant type of humus; in fact, Jenny (1948) reports the existence of a 4-in. layer of raw humus on another group of podzolic yellow soils formed under a similar climate in this region. In highland forest the decomposition constant is much lower, as would be expected with the reduced temperatures. The constants for lowland forest soils are about three times larger than those for savannah soils. The low rate of decomposition in savannah soils is probably connected with the repressive effect which grasses exert on humus mineralization, as shown by the very low levels of nitrate in such soils (see Greenland, 1958, for discussion of this evidence).

No attempt has been made to obtain widely representative figures for the temperate zone, but it is interesting to note that Jenny's figures for oak and pine forests at 5,000 ft. give humus-carbon decomposition constants closely similar to those for highland tropical forests.

Comparison of Decomposition Constants during the Fallow and Crop Phases

'Apparent' cropping-period decomposition constants have been calculated from recorded values for organic-matter changes using the equation $dC/dt = K_c C$, or in the integrated form, $K_c = 1/t \ln C_i/C$, where C_i is the initial soil-carbon content, and C the content after t years of cultivation. These values are given in Table 2. The 'apparent' constant is less than the 'true' constant because no allowance is made in the equation for the return of crop residues. At high rates of

decomposition the difference is not great (cf., for example, Salter and Green, 1933).

For the lowland-forest zone, where crops are grown with the minimum of soil disturbance the constant is similar under fallow vegetation and under crop rotation, but much higher for bare-fallow conditions. For the savannah zone the decomposition constant is much greater during cultivation, a difference due partly to the fact that mineralization is repressed under fallow, and partly to the fact that the savannah soils are thoroughly disturbed during cultivation by annual ridging or mound building. It will be noticed that the results for the decomposition constants for tropical soils during cropping are not frighteningly high, nor greatly different from those for temperate zone soils, which indicates that the loss of organic matter caused by high rates of oxidation at high soil temperatures is not always the primary cause of low organic-matter contents in tropical soils. The effects of low returns of organic matter due to burning and soil erosion are also very important.

The Predicted Increases of Organic Matter and Nitrogen in the Fallow Period

By combining equations (1) and (2) we obtain

$$\frac{dC}{dt} = (f_1 L + f_2 R)\left(1 - \frac{C}{C_E}\right). \qquad (3)$$

C/C_E is of course the fraction of the final equilibrium level to which the profile has been built up. This equation expresses the fact, illustrated in Fig. 2, that, under conditions for which a logarithmic increase can be assumed, the rate of increase of humus declines as equilibrium conditions are approached, $(f_1 L + f_2 R)$ remaining effectively constant. When considering the rate of increase of organic matter and nitrogen in the soil it is therefore very important to decide at what fraction of the final equilibrium level the fallow is operating. It must be clearly realized here that in one fallow period of about 10 years we are concerned with only a relatively small increase in the carbon content of the soil. It is therefore reasonable to regard the rise and fall in the level of carbon with alternate fallow and crop as a fluctuation about a steady level which is a fraction of the virgin level. This is also illustrated in Fig. 2.

The fluctuations curve is shown broken at the end of the cropping phase and start of the fallow phase. This is because some time will usually be required for the natural vegetation to re-establish itself and hence for the production of fresh humified material to reach a level equivalent to that under well-developed vegetation. In the drier parts of the savannah zone the redevelopment of vegetation may take a number of years, particularly if the cropping period is prolonged or erosion occurs. In the more humid tropical areas, however, regeneration of vegetation after a period of cultivation is rapid. Not only are climatic conditions highly favourable to rapid growth but the normal native practice of cultivation leaves many stumps and roots in the ground from which the vegetation can redevelop. Bartholomew *et al.* (1953) have in

fact shown that the amount of fresh green matter in forest vegetation in the Belgian Congo reaches its maximum value only 5 years after the end of cultivation. The increase in the standing vegetation after 5 years is almost all in the woody parts. Hence the rate of increase of humus carbon early in the fallow period is probably not much less than when the fallow vegetation is well developed.

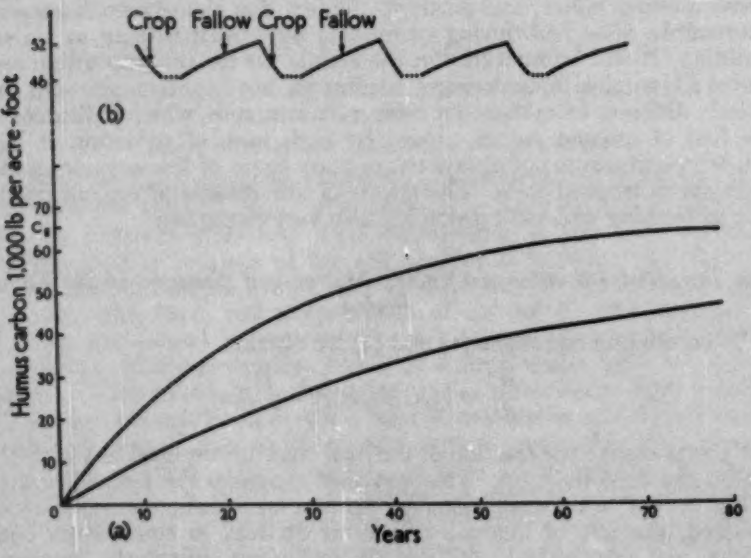

FIG. 2.

In a survey of over 100 profiles in the forests of Liberia, Reed (1951) found that the carbon contents of soils under shifting cultivation were on the average 75 per cent. of those under primary forest. Experience in Ghana of forest soils under increasing pressure of population is that the forest-fallow system breaks down and savannah grasses maintained by annual burning supervene before the carbon content of the profile has dropped to 50 per cent. of the equilibrium level; though with careful control, farming with a forest fallow at this level should be possible. Shifting cultivation is rarely practised at near the virgin level, partly because the labour of clearing mature forest is great and farmers prefer to clear secondary forest that has regenerated sufficiently—rarely over 20 years old. Hence it seems most informative to present in Table 1 the nitrogen increases that may be expected to occur at 75 per cent. of the equilibrium level. The nitrogen increases are readily calculated from the carbon increases if it is assumed that the C/N ratio of the soil at equilibrium persists through the fallow period, and available evidence suggests that it does.

Cropping intensity in savannah varies widely, but it is certain that

in many areas with short fallows of under 5 years the soil carbon is on the average under the 50 per cent. of equilibrium level. For comparison with the forest, increases at the 75 per cent. level are quoted. Those at the 50 per cent. level would be twice as great.

It is seen from Table 1 that during the fallow period in tropical-forest areas the soil-nitrogen increment lies somewhere between 20 and 55 lb. per acre per annum. In the savannah zone the upper limit is between 5 and 14 lb. per acre per annum and in the temperate zone the increment at 75 per cent. of equilibrium is apparently under 11 lb. per annum in both woodlands and grasslands. This nitrogen increment does not of course represent the total annual fixation. Particularly during the early stages of the fallow there is a rapid increase in the amount of nitrogen stored in the vegetation, and in addition losses by leaching and denitrification will be proceeding simultaneously. The analyses of forest-fallow vegetation by Bartholomew *et al.* (1953) and unpublished data of the authors show that the rate of increase in the vegetation is about 100 lb. per acre per annum during the first 5 years of growth, but thereafter falls rapidly to about 10 lb. per acre per annum. There are no satisfactory data available regarding nitrogen losses from tropical-forest soils by leaching and denitrification, but even ignoring such losses it is seen that in favourable circumstances the rate of fixation during the early stage of the fallow may be as high as 150 lb. of nitrogen per acre per annum.

The upper limit of nitrogen gained by plant and soil in humid savannah areas is well below that of the forest. For example at Ejura in Ghana the total nitrogen content of humid fire-climax savannah grasses and other herbs is 36 lb. per acre (Nye, 1958) for one year's growth. In the sub-humid savannah areas the herb vegetation does not contain more than 30 lb. of nitrogen (Weinmann, 1948).

It is interesting to note that in the tropics the relationship between soil organic matter and vegetation type is the reverse of what is found in the temperate zone. In the tropics much the largest addition of organic matter to the soil takes place under forest vegetation, and the soil organic-matter levels tend to be greater than under savannah. In the temperate zone organic-matter production tends to be greater on grassland areas, and it is the grassland soils which have the highest levels of soil organic matter. The mean annual soil-nitrogen increments show a similar inverse relationship (Table 1).

Because of the number of assumptions involved in deriving these results it is very desirable that they should be compared against similar results obtained by direct measurement. Unfortunately very few studies of differences in the organic-matter content of soils when under natural fallow and when cultivated have been reported. One obvious reason for this is that the differences will be relatively small, and unless the same soil is sampled at exactly the same depth and analysed in the same way at successive intervals over a relatively long period, or very closely similar and well replicated sites are compared, then random differences are likely to outweigh differences due to the effects of the fallow. Most studies that have been reported show a failure to appreciate

the importance of these points, as for instance the study of 'chena' cultivation in Ceylon by Joachim and Kandiah (1948).

Another source of confusion in evaluating data on changes in soil humus is that little if any attention has been given to the importance of the equilibrium concept. According to this concept the effect of a fallow on soil organic matter depends as much on the initial organic-matter level of the soil in relation to the equilibrium level under the fallow as on the properties of the fallow itself. This makes it understandable why for example Joachim and Kandiah (1944) can report a large increase of organic matter under an elephant-grass fallow in the forest region of Ceylon (2,000 lb. per acre in 3 years), whereas in similar circumstances in the Congo, du Bois (1957) observed no addition to the soil organic matter from a similar fallow. Clearly the Congo soil must have been at or above its equilibrium level for grassland-fallow conditions. Similarly Popenoe (1957) in Guatamala, with a soil containing 18·0 per cent. carbon in the surface horizon found only insignificant organic-matter changes after forest fallows of 2–5 years. It is therefore evident that the effects of a fallow in increasing soil organic matter can only be judged in relation to the equilibrium level, and unless this is known it is difficult to evaluate the evidence as to the effects of a fallow in this respect.

The best evidence in support of the equilibrium concept is to be found in observations on very young fertile soils, such as the volcanic-ash deposits at St. Vincent studied by Hardy (1939). Here he observed an increase of organic matter in the top 6 in. of soil, under rapidly developing forest vegetation, of 34,000 lb. per acre in a 17-year period. Such a high rate is only to be expected in a soil a long way below its equilibrium level. The rapid increase of organic matter on eroded land planted to legumes, and therefore a rather particular case, observed by Smith, Samuels, and Cernuda (1951) in Puerto Rico is also only to be expected in soil where the organic-matter level is much below equilibrium.

Additional evidence of the validity of the assumptions which have been made is provided by a comparison of the crop: fallow ratio predicted to maintain organic matter with that found in practice. From equation (3) the annual increase in carbon at the 75 per cent. level expressed as a percentage of the final equilibrium level is

$$\frac{dC/dt \times 100}{C_E} = \frac{K_f C_E (1-0{\cdot}75)}{C_E} = 0{\cdot}25\, K_f.$$

The average value of K_f in the lowland forest lies between 5 and 2 per cent. For a value of $K_f = 4$, the increase will amount to 1 per cent. of the equilibrium level per annum. Thus, over a 10-year fallow period the carbon and nitrogen will increase from the region of 70 to 80 per cent. of the equilibrium level. With lower limit values of K_f, or for highland soil or those with excessive rainfall, the percentage increase over the period and therefore the fluctuation about the 75 per cent. level will be reduced.

During the cropping period the annual loss of carbon expressed as a percentage of the equilibrium level will be

$$\frac{dC/dt \times 100}{C_E} = \frac{K_c C_E \times 0{\cdot}75}{C_E} = 0{\cdot}75\, K_c.$$

The ratio of fallow to crop required to maintain a 75 per cent. level is therefore

$$\frac{0{\cdot}75 K_c}{0{\cdot}25 K_f} = 3{\cdot}0 \frac{K_c}{K_f}.$$

It has been shown that for cultivation in forest areas under native practice, which involves only very slight soil disturbance, K_c is similar to K_f. It is thus tentatively predicted that in these areas a fallow:crop ratio of about 3:1 will maintain organic matter and nitrogen at the 75 per cent. level, the period of the fallow being reckoned from the time that a complete vegetative cover is established.

Under the normal practice of shifting cultivation the lengths of crop and fallow periods vary greatly from area to area, and they also vary on the same piece of land with time. In many systems the cropping period merges without definite break into the fallow period. But subject to these limitations a reasonable average for the length of the fallow period in the humid parts of tropical Africa and Asia is ten years, and for the cropping period 2 years. Reed (1951) gives these as the average length

TABLE 2

Humus Carbon Decomposition Constants for Soils under Cultivation Calculated from the Formula $K_c = 1/t \ln C_i/C$, *where* C_i *is the Initial Soil Carbon Content and C the Content after t years of Cultivation*

Soil treatment		Depth of sampling (in.)	Period of cultivation (years)	Decomposition constant, K_c (loss of C per annum %)	Authority
Tropical forest zone—Lowland					
B. Congo	Clean-weeded bare fallow.	20	3	12·8	Beirnaert, 1941
Ghana	Maize, cassava rotation .	12	7	4·7	Nye and Stephens, 1959
Trinidad	Crop rotation with legumes	6	6	2·6	Hardy and Evans, 1945
	Crop rotation with legumes	6	12	1·8	
Savannah zone					
Ghana	Crop rotation . .	12	7	4·0	Nye and Stephens, 1959
Senegal (Sefa)	Continuous groundnuts .	..	6	6·6	Fauck, 1956
Sudan (Zandeland)	Cotton, ground-nuts, eleusine rotation . .	7	6	2·5*	Anthony and Willimott, 1956
Temperate zone					
U.S.A.	Continuous corn . .	7	25	2·8	Klemme and Coleman, 1939
Missouri	Crop rotation . .	7	25	0·8	
France	Crop rotation . .	10	14	1·36	Morel, Richer, and Masson, 1956

* In calculating this constant, results for one trial case which showed an increase of carbon during cultivation have been omitted. If included, the decomposition constant obtained is 1·44 per cent.

of fallow and cropping periods in Liberia, where the organic-matter content under secondary forest is 75 per cent. of that under primary forest. With the allowance to be made for the initial lower rates of litter fall and root production there is fair agreement with the predicted crop-to-fallow ratio. Vine (1954) reports similar data for Nigeria and Peltzer (1948) for the Asiatic tropics. Such periods would therefore seem to be widely representative. Provided soil erosion or invasion by savannah grasses does not intervene and cropping is not continued for more than two or three seasons such systems will probably maintain organic matter quite adequately.

For the savannah zone K_c/K_f is on the average about 4·0 (Table 2). Hence the predicted crop : fallow ratio required to maintain organic matter at about the 75 per cent. of equilibrium level is $3{\cdot}0 \times 4{\cdot}0 = 12{\cdot}0$. At 50 per cent. of the equilibrium level the ratio will be 4·0 : 1. The level of organic matter at which these areas are farmed varies widely, as does the ratio of crop to fallow. However it seems probable that a longer fallow period than in the forest zone is normally required if organic matter is to be maintained at any given fraction of the equilibrium level.

REFERENCES

ANTHONY, K. R. M., and WILLIMOTT, S. G. 1956. Emp. J. Exp. Agric. **24**, 75–88.

BARTHOLOMEW, W. V., MEYER, J., and LAUDELOUT, H. 1953. Publ. Inst. Nat. Agron. Congo Belge, Sér. Sci., No. 57.

BEIRNAERT, A. 1941. Ibid., No. 26.

BIRCH, H. F. 1958. Plant and Soil, **10**, 9–31.

DU BOIS, H. 1957. Bull. Inform. INEAC **6**, 227–41.

ENDREDY, A. S. DE, and MONTGOMERY, C. W. 1954. Trans. 5th Int. Congr. Soil Sci. **3**, 268–73.

FAUCK, R. 1956. Trans. 6th Int. Congr. Soil Sci. **E**, 593–6.

GERMAIN, R., and EVRARD, C. 1956. Publ. Inst. Nat. Agron. Congo Belge, Sér. Sci. No. 67.

GREENLAND, D. J. 1958. J. Agric. Sci., **50**, 82–92,

HARDON, H. J. 1936. Korte Meded. Alg. Proefsta. Landb., No. 18, pp. 24.

HARDY, F. 1939. Trop. Agric. Trin. **16**, 58–65.

—— and EVANS, L. J. C. 1945. Ibid. **22**, 128–37.

HÉNIN, S., and DUPUIS, M. 1945. Ann. Agron. **15**, 17–29.

JENNY, H. 1933. Mo. Agric. Exp. Sta. Bull. 324, pp. 10.

—— 1941. Factors of Soil Formation. McGraw-Hill, New York.

—— 1948. Soil Sci. **66**, 5–28.

—— 1950. Ibid., **69**, 63–69.

—— GESSEL, S. P., and BINGHAM, F. T. 1949. Ibid., **68**, 419–32.

JOACHIM, A. W. R., and KANDIAH, S. 1944. Trop. Agriculturist, **100**, 75–81.

—— and KANDIAH, S. 1948. Ibid., **104**, 3–11.

KLEMME, A. W., and COLEMAN, O. T. 1939. Mo. Agric. Exp. Sta. Bull., No. 405.

LAUDELOUT, H., and MEYER, J. 1954. Trans. 5th Int. Congr. Soil Sci., **2**, 267–72.

MOREL, R., RICHER, A., and MASSON, P. 1956. Trans. 6th Int. Congr. Soil Sci., **B**, 805–10.

MUIR, A., ANDERSON, B., and STEPHEN, I. 1957. J. Soil Sci. **8**, 1–18.

NYE, P. H. 1958. J. W. African Sci. Assoc. **4**, 31–49.

—— and STEPHENS, D. 1959. Soil Fertility in Agriculture and Land Use in Ghana. Ed. A. G. Beattie, Accra.

PELZER, K. J. 1948. Pioneer Settlement in the Asiatic Tropics. Amer. Geog. Soc., Spec. Pub. No. 29.

PERNET, R. 1953. Mem. Inst. Sci., Madagascar, Ser. D, **5**, 251–86.

POPENOE, H. 1957. Proc. Ninth Pacific Sci. Congr., Bangkok.

REED, W. E. 1951. U.S. Dept. Agric., Inf. Bull. No. 66.
ROST, C. O., and ALWAY, F. J. 1921. Soil Sci. **11**, 161–200.
RUSSELL, E. W. 1950. Soil Conditions and Plant Growth. 8th ed. Longmans, London.
SALTER, R. M., and GREEN, T. C. 1933. J. Amer. Soc. Agron. **25**, 622–30.
SANTYANARAYANA, K. V. S., SWAMINATHAN, K., and VISWANATH, B. 1946. Indian J. Agric. Sci. **16**, 316–27.
SMITH, R. M., SAMUELS, G., and CERNUDA, C. F. 1951. Soil Sci. **72**, 409–27.
TROUGHTON, A. 1957. The Underground Organs of Herbage Grasses. Commonw. Bureau Pastures and Field Crops Bull. No. 44.
VINE, H. 1954. Proc. 2nd Inter-Afr. Soils Conf. **2**, 389–412.
WEAVER, J. E., and ZINK, E. 1946. Ecology, **27**, 115–27.
WEINMANN, H. 1948. Rhod. Agric. J. **45**, 119–31.

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INTERACTION OF IRON WITH RAINFALL LEACHATES*

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Summary

Leachates from decomposing leaves of four species of deciduous trees were collected after each rainfall during the months of May to September. Determinations were made of the capacity of these leachates to take up iron from iron-saturated Dowex-50 and to withhold this iron from exchange and/or adsorption by exchange resins saturated with H, Al, Ca, and Mn. For both characteristics the leachates ranked maple > poplar > birch > beech. The capacity of ion-saturated resins to remove iron from iron-enriched leachates was as follows: H > Al > Ca = Mn. This behaviour may be related to the variable thicknesses of the horizons of eluviation and deposition of iron in various podzolic soils. These horizons are, in general, thinner in the strongly acidic Podzol soils than in Grey-Brown Podzolic soils more highly saturated with calcium.

Potentiometric titrations of metal-free and iron-enriched leachates indicated that titratable acid groups were blocked by the added iron. Apparent pK values of metal-free leachates ranged from 3·6 to 3·9, those of iron-enriched leachates, except poplar, from 4·7 to 5·0.

THE hypothesis that substances leached from freshly fallen litter might be of special importance in the translocation processes of sesquioxides usually associated with podzolization has received considerable support during recent years (Bloomfield, 1955, 1957; DeLong and Schnitzer, 1955; Schnitzer and DeLong, 1955). However, much remains to be learned of the nature of the interaction of the organic matter of such leachates and inorganic soil constituents.

This paper reports the capacities of rainfall leachates, derived from decomposing leaves of several deciduous tree species, to take up iron from iron-saturated exchange resins and to retain this iron on subsequent contact with exchange resins saturated with different ions such as are commonly encountered in podzolized soils. In order to throw some light on the nature of iron-organic matter interaction, potentiometric titrations of metal-free and iron-rich leachates were carried out and apparent pK values were evaluated. The findings were related to the known behaviour of iron in certain podzolized soils.

Materials

The leachates studied were derived from the sources listed in Table 1. The soil series are those on which the trees were grown. The Rubicon, Perrot, and Upland series are sandy Podzols, the Rubicon having characteristics of a Ground-Water Podzol. The Grenville is a Brown Forest soil of a clay-loam texture.

Leachates were collected as described by Lutwick *et al.* (1952). Briefly, 8·4 lb. of air-dry whole leaves, gathered in the fall shortly after reaching the soil surface, were exposed in the early spring on wire screens

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TABLE 1

Nomenclature and Description of Materials used as Sources of Leachates

Designation in text	*Description*	*Soil series*
Beech	Leaves of *Fagus grandifolia*	Rubicon
Birch	Leaves of *Betula populifolia*	Uplands
$Maple_o$	Leaves of *Acer saccharum*	Grenville
$Maple_p$	A mixture of leaves of *Acer saccharum* and *Acer rubrum*	Perrot
Poplar	Leaves of *Populus grandidendata*	Rubicon

supported by specially constructed trays in the Morgan Arboretum at Macdonald College. After each rainfall, from early May to the beginning of September, solutions which had passed through these leaves were collected in pails and transported to the laboratory where they were processed as soon as possible to avoid excessive bacterial decomposition. The leachates were brown to light yellow in colour depending on the volume of rainfall.

Methods

Preparation of cation-enriched resins

Dowex-50 (Nalcite HCR), 16–50 mesh mainly in the sodium form, was used in all experiments.

Fe- and Al-resins were prepared by shaking portions of the resin with excess $FeCl_3.6H_2O$ and $AlCl_3.6H_2O$ solution respectively. Saturation of the resin was ascertained by analysis of the supernatant liquid at frequent time intervals until the concentration of the latter remained constant. H-, Ca-, and Mn-resins were prepared by passing an excess of HCl, $CaCl_2.6H_2O$, and $MnCl_2.6H_2O$ solution respectively over portions of resin in glass columns. After saturation, all resins were thoroughly washed with distilled water until the pH of the effluent solution approached that of distilled water.

The degree of saturation of the resin with regard to the various ions was determined by using accurately analysed solutions and proceeding as outlined above. After thorough washing of the resin with distilled water the supernatant or effluent solutions, together with the washings, were analysed for the particular ion. The difference between the amount of metal added initially and that recovered in these solutions was considered to be equal to the exchange capacity of the resin for the metal. The exchange capacity for the H-ion (found, 4·7 m.e./g. of oven-dry resin) was taken as 100 per cent. saturation. The percentage saturation of the resin with regard to the other ions averaged approximately 90 per cent. This means that at least 9 out of 10 exchange sites were occupied by the ions used for saturation.

All resins were used only once in order to avoid complications due to adsorption of organic matter, reduction in exchange capacity, &c. The flow rate ranged between 15 and 25 ml. per hour.

Preparation of H- and Fe-leachates

On reaching the laboratory, one litre of each leachate was passed over 40 ml. of H-resin in 2 × 60 cm. glass columns to remove metallic cations and to provide a more or less uniform starting material. These solutions will be referred to as H-leachates.

After preparation of the H-leachates, 500 ml. of each was passed over 20 ml. of Fe-resin in 1·5 × 40 cm. glass tubes. These solutions will be designated Fe-leachates. The effluent solution was analysed for iron.

Passage of Fe-leachates over resins saturated with various ions

Fifty ml. of each Fe-leachate was passed through 25 ml. burettes containing 2 ml. of H-, Al-, Ca-, and Mn-resin respectively. These experiments were done in duplicate. The effluent solutions were analysed for iron. From the known iron content of the influent solution, the loss of iron was calculated for each leachate. The array of exchange resin columns saturated with the various ions could be likened to the various horizons of a soil profile. An H-resin is thought to simulate the state of affairs in the A_2 horizon of a podzol, a Ca-resin that occurring in the calcium-rich horizons of a Grey-Brown Podzolic or Grey Wooded soil.

Potentiometric titrations

To 25 ml. aliquots of H- and Fe-leachates, dilute standard NaOH solution was added in small increments from a microburette. The solutions were agitated by a stream of purified nitrogen and pH readings were taken after addition of each increment, sufficient time being allowed for equilibration before taking the final reading. A Beckman Model G pH meter with a glass-calomel electrode system was used.

Analytical methods

Organic matter was estimated by diochromate oxidation (Peech *et al.*, 1947) after evaporation of suitable aliquots to dryness on the steam bath. Solids were determined by evaporating aliquots on the steam bath and then drying to constant weight at 105° C. Iron was measured by 2–2′ dipyridyl (Moss and Mellon, 1942), aluminium by ferron (Davenport, 1948), manganese by oxidation with KIO_4 (A.O.A.C., 1950, p. 23), and calcium as the oxalate (Kolthoff and Sandell, 1948, p. 606) after destruction of organic matter by digestion with a mixture of H_2SO_4, HNO_3, and $HClO_4$.

Results and Discussion

Loss of organic matter to resins

By analysis of the influent and effluent solutions from the H- and Fe-resins it was found that no organic matter was lost to the H-resins, whereas up to 8 per cent. was lost to the Fe-resins, the losses varying with the species from which the leachate was obtained.

Fe-beech, Fe-maple$_p$, and Fe-poplar leachate lost no organic matter to the variously saturated resins, whereas Fe-birch and Fe-maple$_o$ lost an additional 10 and 6 per cent. of the original organic matter respectively.

Each 'horizon' constituted the third column through which the leachate had passed and a certain amount of adsorption on the resin particles was to be expected.

Iron uptake from Fe-resin by leachates

Table 2 presents the amounts of iron taken up per unit weight of organic matter for each leachate collected during the season. On the basis of the data the solutions can be grouped into three classes of increasing reactivity: birch and beech < poplar < $maple_p$ and $maple_o$. The proximity of the median to the average indicates a normal distribution of individual measurements around the arithmetic average. The variations of iron uptake with dates of collection could be due to the irregular release of substances with high iron-binding power. There are some differences between species in this respect. For example, the iron uptake of all leachates of collection No. 2, except poplar, was lower than that for collection No. 1. The iron-binding power of $maple_p$ of collection No. 3 increased steeply over that of collection No. 2, while that of the other leachates remained more or less constant. In the case of collection No. 9 the iron uptake by all leachates was very low, while for collection No. 14 $maple_o$ was the only efficient leachate. Until more is known about the organic components in the leachates responsible for this reaction it is not possible to give a satisfactory explanation for these variations.

TABLE 2

Iron Uptake of H-Leachates Collected During the Spring and Summer of 1952

Collection no.	Date of collection	Iron uptake (mg.Fe/g. O.M.)				
		Species				
		Beech	Birch	$Maple_o$	$Maple_p$	Poplar
1	May 7	10·7	7·6	15·0	16·7	17·2
2	12	4·2	4·9	6·7	10·4	18·2
3	21	4·7	4·8	6·1	24·0	15·1
4	26	5·0	2·4	13·3	12·5	11·5
5	June 1	6·0	3·4	15·3	19·0	11·4
6	7	5·2	2·9	15·0	18·5	7·3
7	12	5·0	6·5	18·3	16·8	11·3
8	17	3·6	2·2	10·4	14·4	7·4
9	25	1·8	1·0	8·0	6·8	3·0
10	July 4	7·0	3·6	16·3	16·8	6·4
11	9	6·9	3·6	10·0	12·2	8·6
12	22	4·1	1·9	7·0	5·8	4·6
13	29	4·2	2·2	12·2	10·9	6·0
14	Aug. 6	1·8	1·9	16·4	10·5	..
15	10	6·5	3·2	17·7	12·8	8·0
16	17	5·6	2·2	11·0	10·2	5·8
17	21	4·1	4·2	17·4	10·6	6·5
18	Sept. 1	5·0	2·5	6·7	4·4	..
Average ± S.E.		5·1±0·47	3·4±0·40	12·4±1·00	13·0±1·18	9·3±1·20
Median		5·0	3·1	12·8	12·5	7·7

Losses of iron to resin-'horizons'

During the season Fe-leachates from seven separate collections were passed over the resin-'horizons'. The mean percentages of added iron lost and L.S.D. at P = 0·05 are shown in Table 3.

TABLE 3

Mean Percentages of Iron Lost by Fe-Leachates of Seven Separate Collections to Resin-'Horizons'*

Species	Mean percentage of added iron lost to resins saturated with				L.S.D. (P = 0·05)
	H	Al	Ca	Mn	
Beech	75	66	51	61	8
Birch	86	68	57	58	8
Maple$_a$	67	48	41	44	8
Maple$_p$	79	49	44	46	9
Poplar	79	60	49	52	10
Overall means	77	58	48	52	
L.S.D. (P = 0·05)	N.S.	16	N.S.	N.S.	

* Collection Nos. 1, 2, 3, 5, 10, 11, 15.

Losses to H-resins were for all species significantly greater than those to the other resins. In the case of beech, birch, and poplar, losses to Al-resins were significantly greater than those to Ca-resins. With the two maple leachates, losses to Al-, Ca-, and Mn-resins did not differ significantly from each other although numerically the order was Al > Mn > Ca. Except for the beech leachate there was no significant difference between the amounts of iron lost to Ca- and Mn-resins. The data of Table 3 represent the combined effects of composition and concentration of complexing substance, of pH of resin, and of the 'other' ion.

TABLE 4

pH Values of Untreated H- and Fe-Leachates and of Effluent Solutions from Resin-'Horizons'

Species	pH						
	Untreated	H	Fe	After passage of Fe-leachates over resins saturated with			
				H	Al	Ca	Mn
Beech	5·0	2·9	3·5	3·1	3·6	4·4	4·5
Birch	5·0	2·9	3·6	3·1	3·8	4·0	4·2
Maple$_a$	4·5	3·1	3·8	3·3	3·9	4·5	4·4
Maple$_p$	4·1	2·9	3·6	3·0	3·5	3·8	3·9
Poplar	5·2	2·8	3·5	2·9	3·7	4·5	4·7

In order to get an idea of the pH within each resin-'horizon', pH values of all leachates of collection No. 1 were measured at various stages of the procedure. The data in Table 4 show that after passage over the H-resin, the pH values of the untreated leachates were considerably

reduced. It is reasonable to assume that the pH of H-Dowex-50 is lower than 3·0. However, in our experience the pH of H-leachates was never more than 0·2 pH units below 3·0. This might be due to an appreciable buffering power of the organic matter of these solutions at this pH level. After passage over the Fe-resin the pH values increased in all cases. As far as the resin-'horizons' were concerned, the effluent solutions from H-resins were more acid than those from Al-resins and those from the Ca- and Mn-resins were less acid than the other two. The pH values from the Ca- and Mn-resins were almost identical. It is clear that the pH of the effluent solution depends upon the ion with which the resin is saturated.

With regard to both iron uptake and capacity to hold the added iron against resins saturated with other ions, the order was essentially the same, namely, maple > poplar > beech > birch. This means that decomposing maple leaves released more efficient iron-binding substances than did leaves of the other species.

In terms of capacity to remove iron from Fe-leachates the resin-'horizons', in general, fell in the decreasing order H > Al > Ca = Mn. Iron associated with this type of organic matter should therefore move more deeply into calcareous than acidic profiles. This might explain such observations on the distribution of iron in the profiles of podzolized soils as the following:

(1) the relatively iron-poor and calcium-rich A_2 horizons of Grey Wooded soils generally are considerably thicker than the corresponding horizons in the hydrogen-rich Podzol soils;
(2) the relatively iron-rich B horizons in the calcium-rich Grey-Brown Podzolic soils lie much deeper in the profile than the corresponding horizons in the hydrogen-rich Podzols;
(3) as the upper part of the profiles of Grey-Brown Podzolic soils become less calcium-saturated, a new iron-rich B horizon tends to form at shallow depth.

Potentiometric titration curves

Fig. 1 presents potentiometric titration curves of selected samples of H- and Fe-birch and -$maple_o$ leachates. The Fe-birch and Fe-$maple_o$ solutions were $0{\cdot}34 \times 10^{-6}$ and 3×10^{-6} M in Fe and contained 6·6 and 11·2 mg. of organic matter respectively. The shape of the titration curves of beech and poplar was similar to that of birch while that of $maple_p$ resembled strongly that of $maple_o$. An examination of the curves shows that the titratable acidity up to pH 10·0 of the Fe-leachates was considerably lower than that of the H-leachates, indicating that titratable groups were blocked by the added iron. In case of chelation one would expect the release of an equivalent number of protons per mole of metal taken up. However, as Martin and Reeve (1958) have pointed out, the situation with regard to the chelation of iron is complicated since both the formation of a 3:1 complex and the hydroxide involve a 3-proton release. It is also possible that the iron is held as $Fe(OH)^{++}$, $Fe(OH)_2^{+}$, ferric dimer or partly in the ferrous form, so that one cannot decide on the basis of titration curves which form dominates.

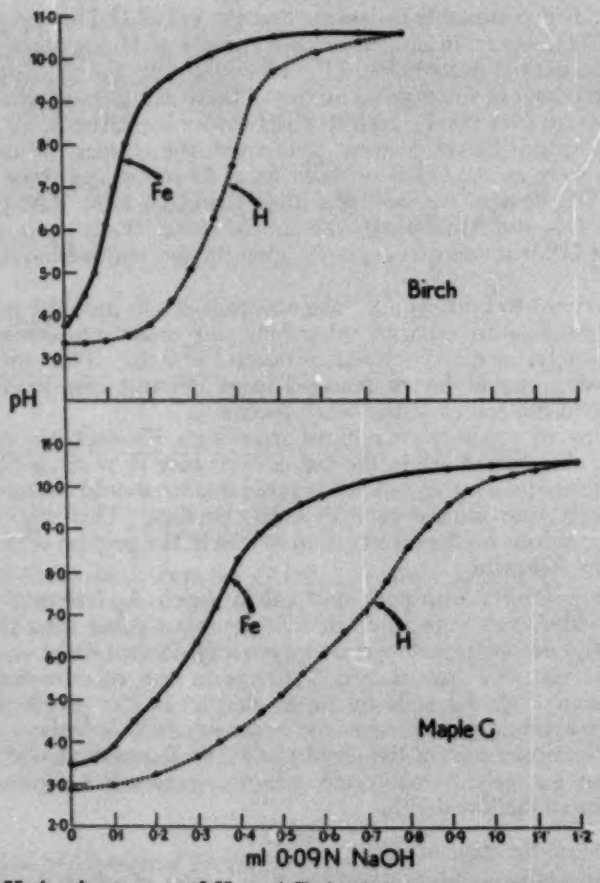

FIG. 1. pH titration curves of H- and Fe-birch and -maple$_6$ leachates (Collection No. 6).

At about pH 9·5 the Fe-leachate curves begin to flatten out and gradually approach those of the H-leachates. This might be interpreted, in the author's opinion, as the beginning of the break-up of the iron-organic matter complex because of increasing hydroxyl-ion concentration according to a reaction such as the following:

$$\text{O.M.-Fe}+3\text{NaOH}\rightarrow\text{O.M.-Na}+\text{Fe(OH)}_3.$$

It is convenient to summarize the results of the titration curves in terms of the apparent pK value of each leachate using the modified Henderson–Hasselbach equation:

$$\text{pH} = \text{pK}_a+n\log\alpha/(1-\alpha),$$

where α = degree of neutralization,
pK_e = exponent of K_e (the empirical value for the acid dissociation constant),
n = empirical constant, which is unity for weak monobasic acids but approaches 2 for some acidic polyelectrolytes.

Fig. 2 shows plots of pH vs. log $\alpha/(1-\alpha)$ for birch and maple$_o$ leach-

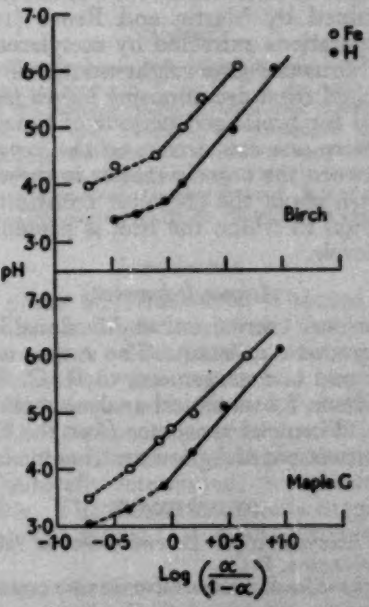

FIG. 2. pH vs. log (α/1−α) for H- and Fe-birch and -maple$_o$ leachates (Collection No. 6).

ates. The shape of the curves for the other leachates were quite similar. From these curves apparent pK values of Fe- and H-leachates were read from the near-linear curves at 50 per cent. neutralization. The value for complete neutralization was set at pH 7·0. No attempts were made to correct for ionic strength since, with the low concentrations involved, this could not have introduced an appreciable error.

TABLE 5

Apparent pK Values of H- and Fe-Leachates (Collection No. 6)

Species	pK_e	
	H-leachates	*Fe-leachates*
Beech	3·85	4·95
Birch	3·75	4·75
Maple$_o$	3·90	4·70
Maple$_p$	3·90	5·00
Poplar	3·55	3·80

Table 5 shows the pK_e values of Fe- and H-leachates of one collection determined on the basis of pH vs. log $\alpha/(1-\alpha)$ plots. The fact that the pK_e values of Fe- were higher than those of H-leachates appears to indicate that mainly acidic groups with low pK_e values were involved in the iron-uptake. Since pK_e values are averages, the blocking of these very acid groups by the added iron caused an increase in the average value. The pK_e values of H-leachates were of the same order of magnitude as those obtained by Martin and Reeve (1958) for metal-free organic matter preparations extracted by acetylacetone from two Australian podzolic B horizons. One might wonder if this means that the organic matter leached from decomposing leaves manages to subsist in podzolic B horizons for prolonged periods of time stabilized by complexed metals. Before one can decide on the type of complex(es) or bond(s) formed between the organic matter in these leachates and iron, more must be known about the chemical constitution of the organic matter and the form(s) in which the iron is present in these solutions at the various pH levels.

Acknowledgements

This investigation was carried out at Macdonald College where the author was a post-graduate assistant. The author is indebted to W. A. DeLong for advice and encouragement, to R. C. Turner for valuable discussion, to J. Friesen for statistical analysis, and to D. E. Coffin for technical assistance. Financial assistance from the Experimental Farms Service, Canada Department of Agriculture, has made this work possible.

REFERENCES

A.O.A.C. Methods of Analysis. 1950. Determination of Acid-soluble Manganese. 7th ed., p. 23. Washington, D.C.

Bloomfield, C. 1955. Leaf leachates as a factor in pedogenesis. J. Sci. Food Agric. **6**, 641–51.

—— 1957. The possible significance of polyphenols in soil formation. Ibid. **8**, 389–92.

Davenport, W. H. 1948. Determination of aluminum in the presence of iron. Anal. Chem. **21**, 710–11.

DeLong, W. A., and Schnitzer, M. 1955. Investigations on the mobilization and transport of iron in forested soils. I. The capacities of leaf extracts and leaf leachates to react with iron. Soil Sci. Soc. Amer. Proc. **19**, 360–3.

Kolthoff, I. M., and Sandell, E. B. 1948. Textbook of Quantitative Inorganic Analysis. Revised ed., p. 606. Macmillan, New York.

Lutwick, L. E., Coldwell, B. B., and DeLong, W. A. 1952. Leachates from decomposing leaves. I. Some general characteristics. Sci. Agric. **32**, 603–13.

Martin, A. E., and Reeve, R. 1958. Chemical studies of podzolic illuvial horizons. III. Titration curves of organic matter suspensions. J. Soil Sci. **9**, 89–100.

Moss, M. L., and Mellon, M. G. 1942. Colorimetric determination of iron with 2-2′dipyridyl and 2-2′-2″ tripyridyl. Ind. Eng. Chem., Anal. ed. **14**, 862–5.

Peech, M., Alexander, L. T., Dean, L. A., and Reed, J. F. 1947. Methods of soil analysis for soil fertility investigations. U.S. Dept. Agric. Circ. 757, p. 5.

Schnitzer, M., and DeLong, W. A. 1955. Investigations on the mobilization and transport of iron in forested soils. II. The nature of the reaction of leaf extracts and leachates with iron. Soil Sci. Soc. Amer. Proc. **19**, 363–8.

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AMORPHOUS IRON OXIDES IN SOILS

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Summary

The identification of amorphous iron oxides in soils has often been based on a sharp exothermic peak at about 320° C. on D.T.A. records. This peak was given by several samples in the present study; in each case it was due to the organic matter present. This was only removed by prolonged treatment with concentrated H_2O_2, though the exothermic reaction was suppressed by using a nitrogen atmosphere in the furnace. The free iron oxides in these same soils are fully accounted for by the crystalline iron minerals present. It is suggested that previous analyses reporting amorphous iron oxide be viewed with caution.

Introduction

SHARP exothermic peaks on Differential Thermal records at about 320° C. have been used by Mackenzie *et al.* (1949) as evidence for the presence of amorphous iron oxides in soils. We have observed similar peaks on the examination of various soils and clays. However, X-ray diffraction analysis of the same soils showed that where free iron oxide was present, goethite and/or haematite were present. Quantitative analysis of many samples by diffraction methods showed that most of the free iron oxide, as chemically determined, could be accounted for by the crystalline iron oxides. The diffraction results suggested that the exothermic reaction observed during D.T.A. was not due to amorphous free iron oxide.

Because of the contradiction between the X-ray analysis and the current interpretation of the D.T.A. results, various treatments were carried out to determine the nature of this commonly observed exothermic reaction at 320° C. In all the soils examined this exotherm was found to be due to organic matter which was difficult to remove by normal pretreatments. Previous identifications of amorphous iron oxide in soils must be viewed with considerable caution as a result of this investigation.

Apparatus and Techniques

The Differential Thermal apparatus has a horizontal furnace based on the design of Norton (1939). A heating rate of 10° C. per minute was maintained by a programmed Kent controller-recorder. The differential temperature was continuously recorded on a Beckman photopen recorder (0·3 μV per mm.) using Pt-Pt 13 per cent. Rh thermocouples. The sample block was of stainless steel and was housed within a cylindrical casing of the same material, the sample, however, was exposed quite freely to the furnace atmosphere. Calcined alumina was used as the inert material and also as a 1:1 diluent with the sample. Generally 0·15 g. of sample was mixed with 0·15 g. of alumina to completely fill the specimen hole in the block.

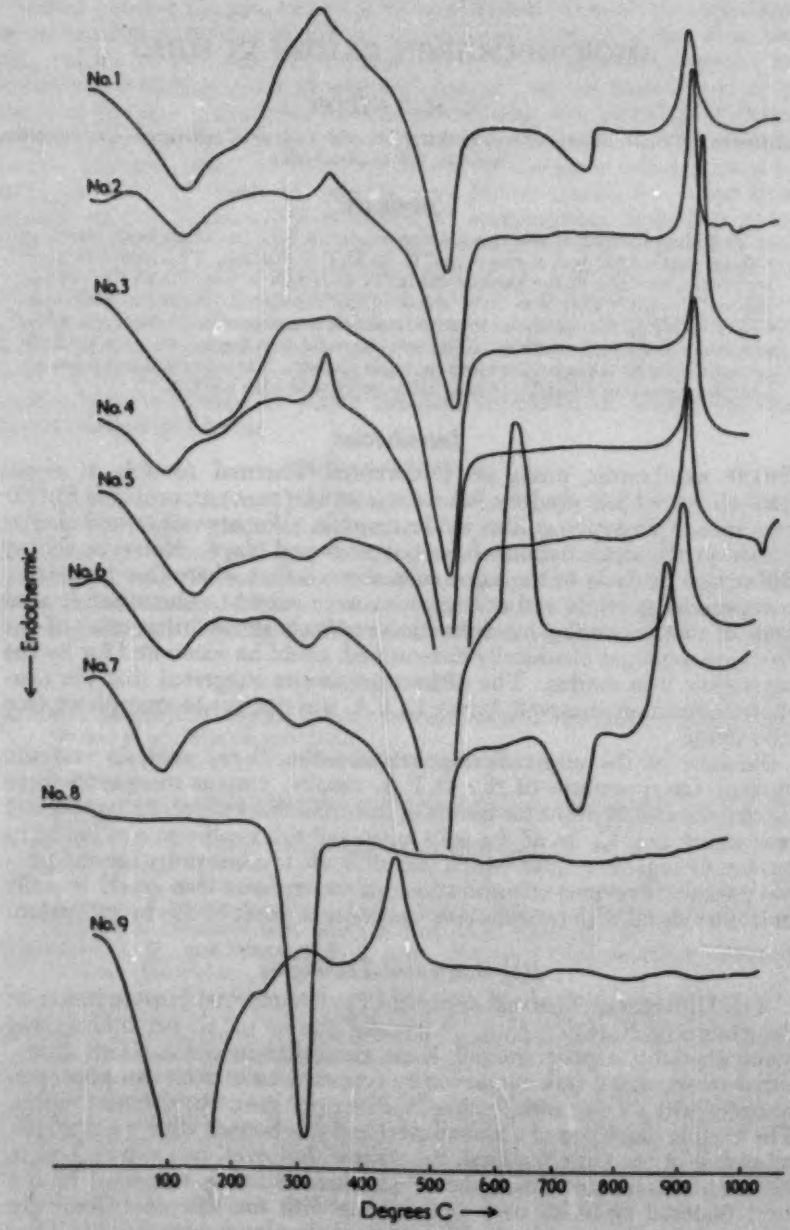

FIG. 1.

(For underline see opposite page)

No attempt was made to bring the clays to a humidity equilibrium before D.T.A. as there was no interest in the low-temperature endotherms.

X-ray powder photographs were obtained on 5·73 and 19-cm. diameter cameras using CoKα radiation. Quantitative estimations of goethite and haematite were made by a modification of the method of Leroux (1953), using a Norelco diffractometer. In the technique employed in this laboratory the absorption coefficients to CoKα radiation were measured directly on an X-ray spectrograph. A fuller report on this technique will be published at a later date. Experience has shown that where the particle size is small enough to give line broadening, quantitative estimations are likely to underestimate the amount present. All iron determinations were made using a fluorescent X-ray spectrograph.

The amount of carbon present in the samples was determined by the dry-combustion method described by Piper (1942). Slight modifications were necessary as the amount of sample available for ignition was often of the order of 200 mg. and the results are considered to be accurate to two significant figures.

Experimental

A terra-rossa soil from Barbados (Hardy, 1950) was chosen for a detailed study. The D.T.A. records for a number of treatments of this soil are shown in Fig. 1; curves 1 and 2 are for the whole soil and its $< 2\ \mu$ fraction. The sharp exotherm at about 320° C. is apparent in curve 2 after the broad exotherm in the whole soil had been removed by the normal oxidation with hydrogen peroxide during the separation of the clay fraction (Piper, 1942). The free-iron-oxide content of the clay, expressed as Fe_2O_3, was 7·5 per cent. and X-ray diffraction analysis showed goethite to be present in an amount which could account for most of this (Table 2). The goethite endotherm on D.T.A. should occur at about 320° C., but it is presumably masked in this sample by the exothermic reaction. Curve 3 shows the effect of free-iron removal by sodium-dithionite treatment of the clay fraction (Mitchell and Mackenzie, 1954). The disappearance of the exotherm at 320° C. after this treatment would suggest that it was due to free iron oxides. However, only a little, if any, of the free iron oxide can be amorphous (Table 2), and yet the exotherm was sufficiently energetic to mask the goethite reaction. Our results and those of Mackenzie (1949) indicate that the goethite endotherm (curve 8) is much larger than the exotherm due to

1. Red Soil, Barbados whole soil.
2. $< 2\mu$ fraction.
3. $< 2\mu$ free iron removed.
4. $< 2\mu$ after boiling for 1½ hours in 1 M citric acid.
5. $< 2\mu$ after 120 hours in 30 per cent. H_2O_2.
6. $< 2\mu$ in nitrogen atmosphere (air readmitted at 610° C.).
7. Whole soil in nitrogen atmosphere.
8. Goethite (Mt. Searle, S.A.).
9. Freshly precipitated ferric hydroxide.

These curves were aligned at 500° C. and the temperature scale shown here is the average derived from the individual curves.

amorphous ferric oxide (curve 9). Therefore, in order to explain the results on this soil clay, the exothermic reaction of amorphous iron oxide would need to be considerably more energetic.

Curve 4 was obtained after boiling the clay for 1½ hours in molar citric acid, which removed about 80 per cent. of the estimated total free iron oxide (Table 1). The exotherm at 330° C. in this curve is larger than in the original clay, presumably due to the removal of the coincident goethite endotherm. The carbon content, however, was not significantly affected by the treatment (Table 1).

TABLE 1

Sample: *Red soil, Barbados* — *Treatment*	*Total iron content* (*as* Fe_2O_3%)	*Carbon content* %
Whole soil (< 270-mesh) .	9·6	1·9
< 2μ separated after normal H_2O_2 treatment . . .	10·5	1·2
< 2μ free Fe_2O_3 removed (by dithionite method) . .	3·0	1·0
< 2μ boiled in 1 M citric acid for 1½ hours . . .	3·9	1·2
< 2μ 120 hours in 30% hydrogen peroxide . .	10·3	0·42

Although the removal of iron oxide by citric acid did not reduce the exotherm, it was found that prolonged treatment by 30 per cent. hydrogen peroxide removed it from the D.T.A. trace. Curve 5, Fig. 1, shows the result of treating the clay for 120 hours with 30 per cent. H_2O_2. The iron-oxide content did not change with this treatment, but the carbon content dropped from 1·2 to 0·42 per cent. In curve 5 the exotherm is replaced by the goethite endotherm.

These results suggest that the exotherm is due to organic matter. To support this a D.T.A. run was conducted in a nitrogen atmosphere (curve 6). The exotherm is completely suppressed while nitrogen is flowing, but occurs more energetically at a higher temperature, 610° C. in this case, immediately air is readmitted to the furnace. Due to the elimination of the exotherm, the goethite endotherm is again observed. In view of the rapid aging of ferric-oxide gels (Gheith, 1952) to goethite and lepidocrocite, a D.T.A. was conducted on the whole soil in an atmosphere of nitrogen (curve 7). The exotherm at 320° C. was eliminated and was replaced by the goethite endotherm. It was concluded that goethite was present in the soil and was not produced by recrystallization during the various pretreatments.

Other soil clays whose D.T.A. records (Fig. 2) showed this exotherm at about 320° C. are listed in Table 2 together with their free-iron-oxide contents, estimated chemically, and iron-mineral contents estimated by X-ray diffraction.

Discussion

From the above results it is concluded that organic matter is responsible for the exothermic peak in the samples examined. The removal of

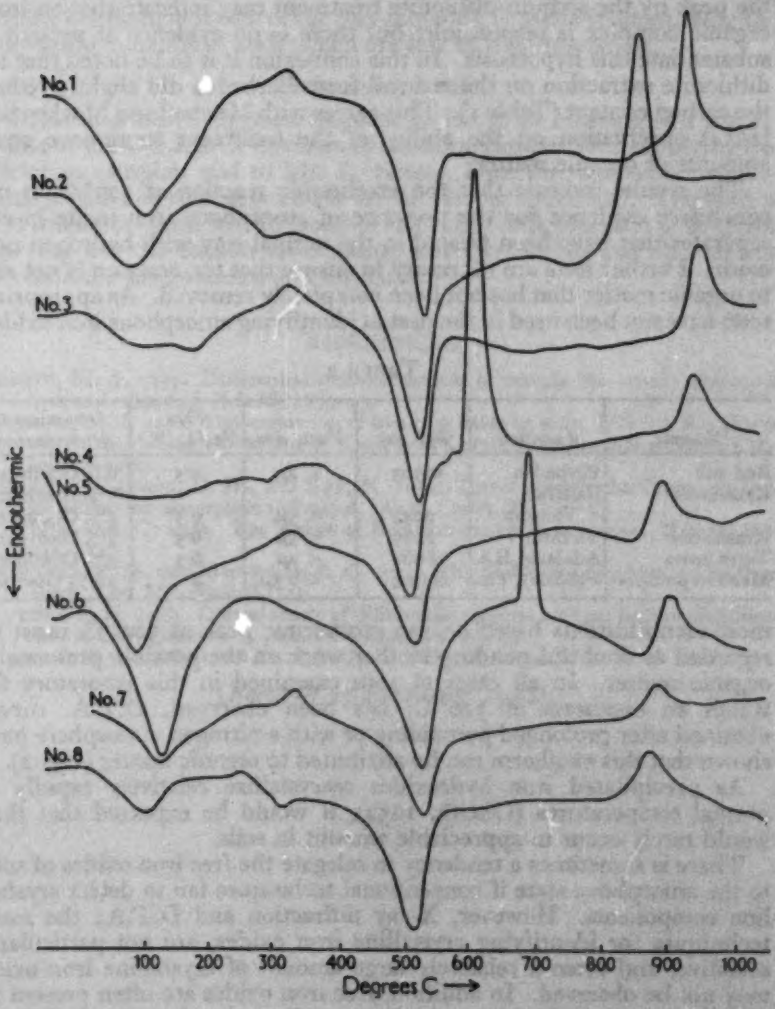

FIG. 2

1. 2042 (Victoria) $< 5\mu$.
2. As above in nitrogen atmosphere.
3. 2087 (Victoria) $< 5\mu$ (after 96 hours H_2O_2).
4. As above in nitrogen atmosphere. Air readmitted 580° C.
5. 16061 (S. Australia) $< 2\mu$.
6. As above in nitrogen atmosphere. Air readmitted 680° C.
7. H53/4 (Tasmania) $< 0{\cdot}5\mu$.
8. As above after 8 days H_2O_2.

These curves were aligned at 300° C. and the temperature scale shown here is the average derived from the individual curves.

the peak by the sodium-dithionite treatment may indicate that an iron-organic complex is responsible, but there is no evidence at present to substantiate this hypothesis. In this connexion it is to be noted that the dithionite extraction on the red soil from Barbados did slightly reduce the carbon content (Table 1). This agrees with Mitchell and Mackenzie's (1954) observation on the ability of the treatment to remove small amounts of organic matter.

The results indicate that the exothermic reaction at 320° C. is not conclusive evidence for the presence of amorphous iron oxide in soil separates that have been treated in the normal way with hydrogen peroxide. Further tests are necessary to ensure that the reaction is not due to organic matter that has not been completely removed. As appropriate tests have not been used in the past in identifying amorphous iron oxides,

TABLE 2

Sample	*Location*	*Ref. no.*	*Part. size*	*Free* Fe_2O_3 (%)	*Iron mineral determination*
Red soil	Barbados	19503	$< 2\mu$	7·5	6% Goethite
Kraznozem	Ballarat, Victoria	2042	$< 5\mu$	9·5	6% Haematite 3% Goethite
Kraznozem	Victoria	2087	$< 5\mu$	6·5	3% Haematite
Terra rossa	Adelaide, S.A.	16061	$< 2\mu$	6·5	3% Goethite
Meadow podzolic	Frodsley, Tas.	H53/4	$< 0{\cdot}5\mu$	4	3·5% Goethite

most identifications based on the exothermic peak at 320° C. must be regarded as doubtful pending further work on the possible presence of organic matter. In all cases of soils examined in this laboratory for which an exotherm at 320° C. has been observed, D.T.A. curves obtained after prolonged peroxiding or with a nitrogen atmosphere have shown that this exotherm can be attributed to organic matter (Fig. 2).

As precipitated iron hydroxides recrystallize relatively rapidly at normal temperatures (Gheith, 1952), it would be expected that they would rarely occur in appreciable amount in soils.

There is sometimes a tendency to relegate the free iron oxides of soils to the amorphous state if conventional techniques fail to detect crystalline components. However, X-ray diffraction and D.T.A., the main techniques for identifying crystalline iron oxides, are not particularly sensitive, and often a relatively large amount of crystalline iron oxide may not be observed. In addition, free iron oxides are often present in two, three, or even four forms in the one soil, so that detection is difficult if the total amount is not large. Commonly, iron-oxide minerals in soils have a crystal size sufficiently small to cause considerable line broadening of their X-ray diffraction lines and this reduces further the sensitivity of the technique.

In attempting to identify the chemically determined free iron oxides, it must be remembered that certain iron-rich clay minerals may yield considerable amounts of iron during treatment for the removal of free iron (Haldane, 1956). A concentration procedure suggested by Norrish,*

* Private communication.

a hydrofluoric-acid attack of the clay minerals, is useful in identifying the iron-oxide minerals of soils which are low in free iron oxide.

Acknowledgements

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REFERENCES

GHEITH, M. A. 1952. Differential thermal analysis of certain iron oxides and oxide hydrates. Amer. J. Sci. **250**, 677–95.

HALDANE, A. D. 1956. Determination of free iron oxide in soils. Soil Sci. **82**, 483–9.

HARDY, F. 1950. Soils of Barbados. Caribbean Commission Reports on Soils Conference 1950.

LEROUX, J., LENNOX, D. H., and KAY, K. 1953. Direct quantitative X-ray analysis by diffraction-absorption technique. Anal. Chem. **25**, 740–3.

MACKENZIE, R. C. 1949. The nature of free iron oxides in soil clays. Nature, **164**, 244.

MITCHELL, B. D., and MACKENZIE, R. C. 1954. The removal of free iron oxides from clays. Clay Min. Bull. **2**, 115.

NORTON, F. H. 1939. Critical study of differential thermal method for the identification of clay minerals. J. Amer. Ceramic Soc. **22**, 54.

PIPER, C. S. 1942. Soil and Plant Analysis. Univ. of Adelaide.

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DETERMINATION OF ORGANIC CARBON IN SOIL AND PLANT MATERIAL

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Summary

A wet-oxidation technique for determining organic carbon in soil, plant material, and aqueous plant extracts is described. The oxidation is carried out by heating the soil or plant sample (containing 50–100 mg. carbon) with a mixture of potassium dichromate, sulphuric, and phosphoric acids for 10–15 min., and the carbon dioxide liberated is determined gravimetrically after absorption in soda-lime. With slight modifications, the method has proved useful for the determination of carbon in plant extracts and would also appear suitable for a soil extract. A method is described for the removal of carbonates without loss of organic carbon. It is shown that heating a wet soil at 105° C. causes considerable loss of organic carbon. Inert carbonaceous material, such as coal or charcoal, is oxidized by this wet-digestion method, thus producing erroneously high results for the carbon content of soil organic matter.

The method is at least as accurate as the conventional dry-combustion technique, and is less time-consuming, only one hour being required for a determination. The apparatus is of simple design and with the exception of the needle valve can be readily constructed from normal laboratory glassware. The method can deal with fairly large samples of materials, thus preserving an essential feature of established macro-methods.

This technique of determining carbon is convenient for the fairly rapid analysis of soils and plant materials where an accurate total-carbon value is required.

Introduction

THE dry-combustion method of determining organic carbon in soil and plant material has been recognized as the standard technique for assessing the accuracy of other methods. In this technique the organic material is heated to a high temperature in a stream of carbon-dioxide-free air and the carbon dioxide produced by combustion of the organic carbon is absorbed in alkali and determined either gravimetrically or titrimetrically. Several modifications of this method have been in use for many years and give admirable results with most organic materials. A recent semi-micro modification has been described by Rickson (1948) in which the time required for the determination of carbon has been considerably reduced without loss of accuracy.

Rapid titration methods in which the soil organic matter is oxidized by potassium dichromate in sulphuric acid and the amount of unreduced dichromate remaining determined by titration with ferrous ammonium sulphate (e.g. Walkley and Black, 1934; Schollenberger, 1927, 1945; Allison, 1935) are sufficiently accurate for approximate work on soils of the same type. Unfortunately the methods based on this principle do not give complete oxidation of the soil organic matter and cannot be used with soils of high carbon content or with soils containing organic matter of widely varying composition. They have been used by some workers (e.g. Allison, 1935) to discriminate to a certain extent between the

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relatively inert carbon in materials such as coal, charcoal, and cinders and the carbon of soil organic matter. Results presented in this paper show that this discrimination can be unreliable in certain circumstances.

The determination of organic carbon in soils by wet oxidation of the organic matter has been described by Bremner (1949) and by Cornfield (1952). Both workers employed the Van Slyke and Folch oxidizing agent, which consists of a mixture of chromic, phosphoric, sulphuric, and iodic acids. Bremner used the Van Slyke-Niel manometric apparatus to measure the carbon dioxide produced on oxidation and Cornfield employed a purification train and absorbed the carbon dioxide in a soda-lime tube. The method used by Bremner, although accurate, allows the use of only very small samples of material, which is often a serious disadvantage when dealing with soil and plant material.

It was desirable to obtain a method of wet oxidation which was at least as accurate as the dry-combustion technique but simpler and less time-consuming in practice. The method of wet oxidation described by Clark and Ogg (1942) appeared to be suitable, but in practice their technique of absorbing the carbon dioxide was found to be inconvenient. However, a combination of their wet-oxidation method with a standard purification train and gravimetric determination of the carbon dioxide after absorption proved to be satisfactory not only for the determination of carbon in soils and plants, but also for analysis of aqueous extracts of these materials. This paper describes the apparatus and the procedure used for the determination of organic carbon by wet oxidation of soils and plant materials.

Apparatus

The apparatus used in this modified combustion method is represented diagrammatically in Fig. 1. The basis of the method is that the organic material is oxidized by heating with a mixture of potassium dichromate, sulphuric and phosphoric acids and the carbon dioxide evolved is freed from possible impurities such as oxides of sulphur or nitrogen and finally dried before being absorbed in weighed soda-lime tubes.

The tube A is filled with soda-lime ('Carbosorb', 4–10 mesh self-indicating granules). The digestion apparatus, shown as B in the diagram, consists of a 50-ml. separating funnel (1), the shortened stem of which fits by means of a B 14 ground-glass joint into the mouth of a similar funnel (2), whose lengthened stem fits by means of another B 14 ground-glass joint into a 50-ml. distillation flask (3). The taps of each separating funnel are lubricated with phosphoric acid. The bulb of the second separating funnel has a side connexion to the tube A through which the carbon-dioxide-free air passes into the digestion flask. The oxidation is carried out by means of a sulphuric-phosphoric acid mixture with potassium dichromate. The acid used for each determination is stored until required in the first separating funnel (1). A small bulb-type water condenser, C, is connected to the side arm of the digestion flask to remove a large part of the water vapour which distils off from the boiling digestion mixture. Tube D contains small pieces of zinc wire, which remove oxides of nitrogen or sulphur from the gas stream. The

gas is dried by passing through anhydrous magnesium perchlorate which is contained in tubes E and F and finally by bubbling through about 20 ml. of concentrated sulphuric acid contained in a 125-ml. Dreschel bottle, G.

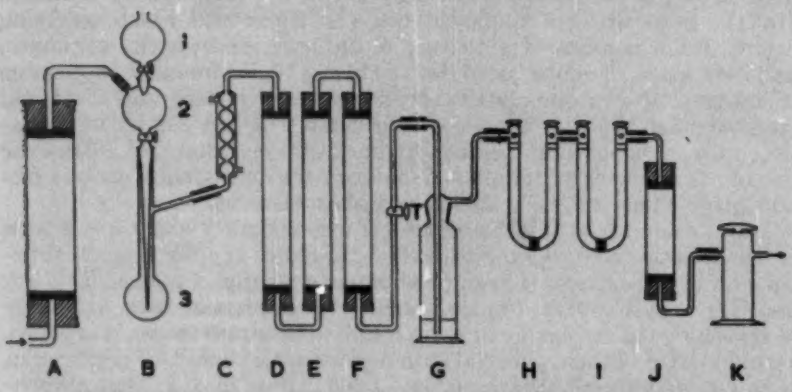

FIG. 1. Diagram of apparatus for determination of carbon in soil and plant materials by wet oxidation.

The dry purified air and carbon dioxide now passes through 2 U-tubes H and I fitted with taps, the left arm of each tube (see diagram) containing soda-lime ('Carbosorb' 10–16 mesh self-indicating granules) and the other arm containing anhydrous magnesium perchlorate. During the absorption of carbon dioxide by soda-lime, water is produced which is absorbed in the magnesium perchlorate. Air is drawn through the apparatus by means of a water pump and it is essential to use a needle valve K (as supplied by A. Gallenkamp) accurately to control the air flow. To prevent entry of water vapour into the U-tubes from the water pump a calcium-chloride tube J is placed between the needle valve and the second U-tube I. A tap, T, which controls the passage of air through the apparatus is situated between the second drying tube F and the Dreschel bottle G and when closed not only prevents passage of air but also eliminates the possibility of any back pressure causing the concentrated sulphuric acid to be sucked back into the magnesium perchlorate. All glass-to-glass joints, other than the ground-glass fittings, are made by using thick-walled 3-mm.-bore pressure tubing.

Reagents

1. Soda lime. 'Carbosorb' (*a*) 4–10-mesh self-indicating granules, B.D.H.; (*b*) 10–16-mesh self-indicating granules, B.D.H. (for use in absorption tubes).
2. Magnesium perchlorate, anhydrous.
3. Analar potassium dichromate, powdered or small crystals.
4. Zinc wire in pieces not more than 1 cm. in length.
5. Concentrated sulphuric acid, Analar.

6. A mixture of 600 ml. of concentrated sulphuric acid and 400 ml. of 85 per cent. phosphoric acid. This mixture is the digestion acid.

Procedure

A sample of soil or organic material (ground to pass a 60-mesh or finer sieve) containing 50–100 mg. carbon is weighed into a dry digestion flask and mixed with 3–4 g. of potassium dichromate and 3 ml. of water. For mineral soils 2–5 g. of soil is usually sufficient, and with peat soils or plant materials 0·2–0·5 g. is satisfactory. The flask is placed in position as shown in the diagram, and 25 ml. of the mixed digestion acid is poured into the upper separating funnel (I), with its tap in the closed position. The Dreschel bottle G is connected to the calcium-chloride tube J, by-passing the U-tubes H and I, the water pump turned on, tap T placed in the 'on' position, and a stream of air slowly drawn through the apparatus for about 30 minutes to sweep out all traces of carbon dioxide. Tap T is turned off and the U-tubes, previously weighed against a similar counterpoise tube, are then placed in position, their taps opened, and air is again drawn through the whole train, while the digestion acid in the separating funnel (I) is slowly run into the flask. The oxidation of the organic material begins almost immediately and once the initial vigorous reaction has subsided the digestion flask is heated for 10–15 min. by means of a micro-bunsen burner. Air is drawn through the apparatus at a rate of about 30–35 ml. per minute, which is approximately 120 bubbles per minute when measured in the sulphuric acid in the Dreschel bottle. The initial absorption of the carbon dioxide by the 'Carbosorb' in the first U-tube H is accompanied by liberation of heat and by a marked change in colour of the 'Carbosorb'. Air is passed through the apparatus for at least 45 min. after the first sign of this absorption, and at the end of this period of time the tap T and those on the U-tubes are turned off and the U-tubes are reweighed, the weight of carbon being calculated from the amount of carbon dioxide absorbed. In practice the second U-tube I hardly changes in weight until the first tube H is nearing exhaustion. If the subsequent determination is performed immediately after removing the previous digestion flask it is not necessary to sweep out all the air from the apparatus as for the first determination since the amount of carbon dioxide introduced in the 50 ml. flask is so small as to be negligible. Periodically blank determinations are carried out using the above procedure in which no organic material is placed in the digestion flask and standard determinations are made using sucrose as the source of carbon. The whole operation of one determination takes about 1 hour as compared with 3–4 hours for the standard dry-combustion technique.

Results

Time of digestion

To determine the time of digestion required to oxidize all the organic matter of the soil or organic material the carbon contents of several soils and plant materials were determined by the recommended procedure, except that the oxidation mixture was heated for different periods of

TABLE 1

Carbon Contents of Various Materials as Determined After Different Periods of Digestion by the Wet-Oxidation Technique

(Carbon results are expressed on a moisture-free basis)

Material	*Time of heating (min.)*	*Carbon %*
Mineral soil 1	5·0	3·00
,,	6·5	3·14
,,	8·0	3·15
,,	9·5	3·16
,,	12·0	3·16
Mineral soil 2	5·0	2·68
,,	6·5	2·78
,,	8·0	2·84
,,	9·5	2·85
,,	12·0	2·86
Organic soil (peat)	5·0	37·25
,,	6·5	37·60
,,	8·0	37·78
,,	9·5	37·80
,,	12·0	37·81
Dried grass meal	5·0	42·02
,,	6·5	42·32
,,	8·0	42·39
,,	9·5	42·43
,,	12·0	42·44

time. Some of the results are given in Table 1. In all samples of soil or plant materials the oxidation was practically complete after heating for 10 min.

Comparison of wet- and dry-combustion techniques

The results obtained on some soils and organic materials by this wet-oxidation method were compared with those by a standard dry-combustion technique (Table 2). The dry-combustion results were obtained by using the method described by Piper (1944). The determination of carbon in soils and plant materials by the wet-combustion method gave results almost identical to those obtained by the dry-combustion method and for these materials the technique was therefore considered satisfactory.

Interference due to inorganic carbon compounds

In all methods of determining the carbon content of soils or organic materials that are based on the measurement of carbon dioxide evolved on oxidation, the presence of carbon as carbonates interferes with the determination. This inorganic carbon must either be removed or determined separately and subtracted from the total carbon. It is preferable to remove carbonate beforehand since a separate determination of the carbonate present introduces another possible source of error. The

TABLE 2

Organic Carbon Content of Soils and Organic Materials as Determined by the Wet-Oxidation and Dry-Combustion Methods

(All results are expressed on a moisture-free basis)

Material	*Carbon % Dry-combustion method**	*Carbon % Wet-oxidation method**
Peat	37·67, 37·71, 37·74 | 37·71	37·80, 37·72, 37·65 | 37·72
Mineral soil	0·66, 0·65, 0·68 | 0·66	0·63 0·65, 0·67 0·64, 0·68 0·66 | 0·65
Mineral soil	0·73, 0·74, 0·70 | 0·72	0·72 0·74, 0·71 0·70, 0·72 | 0·72
Mineral soil	3·26, 3·28, 3·25 | 3·26	3·25 3·26, 3·23 3·25, 3·28 | 3·25
Surface grass 'mat'	40·50 40·43, 40·25 40·40, 40·19 40·32 | 40·35	40·30 40·38, 40·48 40·32, 40·21 40·26 | 40·32
Dried grass meal	43·63, 43·57, 43·69 | 43·63	43·63 43·67, 43·69 43·70, 43·59 | 43·66
Sucrose (42·10 per cent. C calc.)	42·05, 42·16, 42·11 | 42·11	42·09 42·04, 42·12 42·06, 42·11 | 42·08

* Results of replicate analyses are given to show the variation between determinations.

only reagent suitable for the preliminary destruction of carbonates is sulphurous acid, as excess is easily removed after treatment by evaporation at room temperature. The usual method for removal of carbonate has been to weigh the soil sample into a boat, add sulphurous acid, and after a few hours remove the excess acid by heating the boat on a steam bath or by leaving it at 105° C. for several hours. The treatment is repeated until all carbonate has been removed. This method has disadvantages in that some loss of volatile carbon compounds may occur during the heating and there is a possibility of mechanical loss during repeated evaporations in a small boat. In preliminary experiments it was found that the carbon content of soils containing calcium carbonate was always slightly lower when the carbonate had been removed by heating during evaporation of the sulphurous acid than when no heat had been applied. Further tests were carried out on five mineral soils to determine the loss of carbon when excess sulphurous acid was evaporated by heating at 105° C. for 16 hours and when the excess acid was removed at room temperature in a vacuum desiccator. In each soil there

TABLE 3

Organic Carbon Contents of Soils as Determined after Removal of Excess Sulphurous Acid by Heating at 105° C. for 16 Hours or by Evaporation in a Vacuum Desiccator

(All results are expressed on a moisture-free basis)

Material	$CaCO_3$ %	Carbon %	
		Vacuum desiccator	*Heating 105° C.*
Soil 3 . .	7·08	3·21	3·08
„ 4 . .	1·82	2·24	2·05
„ 6 . .	1·19	4·44	4·05
„ 9 . .	46·80	2·47	2·20
„ 10 . .	0·02	0·98	0·90

was a considerable loss of carbon when the sulphurous acid was evaporated by heating in an oven at 105° C. It was of interest to determine if this loss was simply due to loss of volatile organic matter or due to decarboxylation of soil organic matter by the sulphurous acid. This was tested by determining the loss of carbon in three soils which contained no carbonate, when they were heated with a similar volume of water instead of sulphurous acid. The results (Table 4) show that heating with water or sulphurous acid caused considerable loss of carbon. Bremner (1949) also found a loss of carbon on heating a soil-sulphurous acid mixture overnight at 105° C. and recommended that the excess acid should be removed by treatment in a vacuum desiccator.

TABLE 4

Carbon Content of Soils as Determined after Evaporating Sulphurous Acid or Water in a Vacuum Desiccator or by Heating at 105° C. for 16 Hours

(All results are expressed on a moisture-free basis)

Soil	Carbon %				Carbon* % No H_2O or H_2SO_3	
	H_2O *treatment*		H_2SO_3 *treatment*			
	Heating 105° C.	*Vacuum desiccator*	*Heating 105° C.*	*Vacuum desiccator*	*Wet oxidation method*	*Dry combustion method*
1	3·04	3·15	3·04	3·14	3·16	3·15
2	2·76	2·88	2·73	2·86	2·86	2·88
5	5·01	5·14	4·83	5·12	5·15	5·13

* Carbon contents of soils without water or sulphurous acid treatment, as determined by wet-oxidation and dry-combustion methods.

One disadvantage of the sulphurous-acid method of removing carbonates before determining organic carbon in soils was that it was difficult to estimate when the removal of the carbonates was complete. To obtain information on this, a carbonate-free soil, to which had been added increasing amounts of calcium carbonate (100-mesh), was treated with varying amounts of 5 per cent. sulphurous acid (in 5 ml. additions).

When there appeared to be no further effervescence on addition of sulphurous acid, the acid treatment was stopped and the carbon content of the soil determined after evaporation of excess acid in a vacuum

TABLE 5

Carbon Content of a Soil Containing Varying Amounts of Added Calcium Carbonate as Determined After Treatment with Different Volumes of 5 per cent. Sulphurous Acid

Wt. of soil (*g.*)	*Wt.* $CaCO_3$ *added* (*g.*)	*Vol. of 5%** H_2SO_3 *used* (*ml.*)	*Carbon* %
2·0	0	0	2·85
2·0	0	10	2·87
2·0	0·02	10	2·88
2·0	0·10	10	2·85
2·0	0·20	20	2·85
2·0	0·40	25	2·88
2·0	0·60	25	2·86
0	0·60	25	0·0

* The volumes of 5 per cent. sulphurous acid quoted here were added in 5 ml. amounts. Each addition was evaporated in a vacuum desiccator before adding the next 5 ml. of acid.

desiccator at room temperature. The results (Table 5) show that the sulphurous-acid treatments removed all the added calcium carbonate. The calcium carbonate used in this experiment was of reagent grade and was finely powdered and comparatively soft, whereas in some soils calcium carbonate occurs as hard particles or rock fragments which may not be so readily attacked by the sulphurous acid as the pure chemical reagent used in this experiment. Magnesium carbonate is even more insoluble in acids than calcium carbonate, so that special attention should be given to fine grinding and to the time of reaction of the soil with the sulphurous acid if magnesium carbonate is suspected of being present.

The procedure, adopted for the removal of carbonates before determining the organic carbon by wet oxidation, was therefore as follows. The normal amount of soil, containing carbonate, was weighed into a dry digestion flask (B, 3, fig. 1) and 5 ml. of 5 per cent. sulphurous acid added. After shaking for a few minutes the flask was placed in a vacuum desiccator, containing sodium-hydroxide pellets in addition to desiccating agent, thoroughly evacuated on a pump, and allowed to stand overnight. This was usually sufficient to evaporate the acid completely. When further acid was required the whole process was repeated until the carbonate was completely removed. The soil remaining in the flask was now treated in the manner already described for determining the organic carbon.

Effect of coal or charcoal on the determination of organic carbon in soil

Many soils contain either coal or charcoal and the presence of either vitiates the accurate determination of the carbon content of the soil

organic matter. No method has yet been devised to overcome this difficulty. Rapid dichromate-titration methods have been employed by some workers (Allison, 1935) to discriminate between the relatively inert carbon of coal, charcoal, or cinders and the carbon of soil organic matter. In the course of other work in which the rapid titration method of Schollenberger, as modified by Allison (1935), was used to determine soil carbon an experiment was carried out to investigate the effect on the carbon determinations when known amounts of coal or charcoal were added to a soil. In this investigation samples of coal and charcoal were ground to pass a 100-mesh sieve and added at two levels to the weight of soil normally used in this technique before the carbon determinations

TABLE 6

*Effect of Coal and Charcoal on the Determination of the Carbon of Soil Organic Matter by a Modified Schollenberger Technique**

	Carbon determined (mg.)
Soil (500 mg.)	11·05
Soil (500 mg.)+coal (5 mg.)	15·50
Soil (500 mg.)+coal (15 mg.)	23·75
Soil (500 mg.)+charcoal (5 mg.)	11·45
Soil (500 mg.)+charcoal (15 mg.)	11·55

* Modification of Schollenberger's method by Allison (1935).

were performed. The results, given in Table 6, showed that coal had a very pronounced effect on the carbon determination whereas the effect of charcoal, although positive, was much smaller. Thus the presence of either of these materials in soil produced erroneously high values for the carbon content of soil organic matter when determined by this technique. These results are not in agreement with those of Allison (1935), who found that this method of determining carbon in soils was not affected by the presence of inert carbonaceous material such as cinders. Since Allison's modification of Schollenberger's method was so seriously affected by coal and charcoal, it was essential to ascertain if these materials affected the determination of carbon by the wet-oxidation method described in this paper. The carbon content of a soil known to contain no detectable amounts of coal or charcoal was determined on 2-g. samples, and then on similar samples containing different amounts of added coal (100-mesh). During prolonged digestion of the soil-coal mixture it was noticed that carbon dioxide was evolved for a longer period than was usually necessary to oxidize all the soil organic matter. This suggested that the oxidation of the coal under these conditions was a slow process and that prolonged digestion would continue to oxidize the coal and so produce a slow evolution of carbon dioxide. This was confirmed by performing an oxidation on coal and following the carbon dioxide evolved on heating for a period of time greater than that required to oxidize soil organic matter. The results of this experiment, together with those of a similar one carried out on a sample of soil with varying amounts of added coal, are given in Table 7.

TABLE 7

Carbon, Evolved as Carbon Dioxide, on Wet Oxidation of Coal, Soil, and Coal-soil Mixture for Various Periods of Time

Material	*Time of heating (min.)*	*Carbon (evolved as CO_2) (mg.)*
Coal (200 mg.)	5·0	39·6
Coal (200 mg.)	10·0	57·2
Coal (200 mg.)	15·0	70·6
Coal (200 mg.)	20·0	80·7
Coal (200 mg.)	25·0	87·7
Soil (2 g.)	5·0	60·0
Soil (2 g.)	6·5	62·9
Soil (2 g.)	8·0	63·0
Soil (2 g.)	9·5	63·1
Soil (2 g.)+coal (50 mg.)	3·0	91·6
Soil (2 g.)+coal (50 mg.)	6·0	101·0
Soil (2 g.)+coal (50 mg.)	9·5	106·2

With this soil, oxidation of the soil organic matter was practically complete after heating for 6·5 min. whereas, when a small amount of coal was present, carbon dioxide was still evolved at a considerable rate even after heating for 9·5 min. On heating coal alone the oxidation was still proceeding after 25 min. digestion. Coal is thus only slowly oxidized by the wet-digestion procedure and when present in soil it will obviously interfere seriously with the determination of the carbon of the soil organic matter. This slow oxidation and evolution of carbon dioxide on prolonged digestion of a soil by the method described here provides a useful indication that the sample contains considerable amounts of coal or other inert carbonaceous material.

It is quite evident from the foregoing results that the presence of coal in soil completely vitiates the determination of the carbon content of the true soil organic matter. The standard dry-combustion technique is also open to this criticism since all forms of carbon are completely oxidized in this method. It is very doubtful if an oxidizing agent exists which will specifically oxidize the carbon of soil organic matter and not decompose any inert carbonaceous material such as coal or charcoal in the process.

Determination of carbon in aqueous extracts of soils and plant materials

For the determination of the carbon content of organic material in aqueous solution it has been customary to evaporate the solution to dryness before analysis. In water extracts of soils or plant materials evaporation could lead to loss of carbon, as it has already been shown in this work that heating a soil-water mixture at 105° C. for several hours causes a loss of carbon. It is advantageous, therefore, to be able to use a technique in which it is possible to determine carbon in aqueous extracts by direct oxidation without previous evaporation.

The wet-oxidation technique has proved useful in this respect as it was found possible by only a slight modification to determine the carbon

content of aqueous extracts of soils or plant materials. The modifications of the method necessary were the use of a 100-ml. digestion flask instead of a 50-ml. flask and the use of double quantities of potassium dichromate and digestion acid when the volume of solution being analysed was greater than 6 ml. The results of an experiment using increasing dilutions of aqueous solutions of sucrose, aspartic acid, and Quebracho-wood extract are given in Table 8. The Quebracho extract used was made by re-dissolving the solid material obtained after evaporation of a water extract of Quebracho wood.

TABLE 8

Carbon Contents of Aqueous Solutions of Sucrose, Aspartic Acid, and Quebracho Extract as Determined by the Wet-Oxidation Method

Material	*Carbon (theoretical) (mg.)*	*Vol. of extract (ml.)*	*Vol. of digestion acid (ml.)*	*Wt. $K_2Cr_2O_7$ (g.)*	*Carbon found (mg.)*	*Carbon recovery (%)*
Sucrose	84·2	3*	20	3–4	83·6	99·4
,,	84·2	6	20	3–4	84·2	100·0
,,	84·2	12	40	6–8	83·9	99·7
,,	84·2	18	40	6–8	83·6	99·4
Aspartic acid	72·2	3*	20	3–4	71·6	99·3
Aspartic acid	72·2	18	40	6–8	71·4	98·9
Quebracho extract (0·200 g.)	..	3*	20	3–4	103·6	..
Quebracho extract (0·200 g.)	..	18	40	6–8	103·9	..

* Volume of water (3 ml.) is that used in normal recommended procedure for wet oxidation.

These results suggest that the wet-oxidation method can be used quite satisfactorily to determine the organic carbon present in aqueous solution without previous evaporation to dryness, provided the concentration of carbon in solution is not less than 5·75 mg. C per ml.

REFERENCES

ALLISON, F. E. 1935. Soil Sci. **40**, 311.
BREMNER, J. M. 1949. Analyst, **74**, 492.
CLARK, N. A., and OGG, C. L. 1942. Soil Sci. **53**, 27.
CORNFIELD, A. H. 1952. J. Sci. Fd. Agric. **3**, 154.
PIPER, C. S. 1944. Soil and Plant Analysis. University of Adelaide.
RICKSON, J. B. 1948. Analyst, **73**, 268.
SCHOLLENBERGER, C. J. 1927. Soil Sci. **24**, 65.
—— 1945. Ibid. **59**, 53.
WALKLEY, A., and BLACK, I. A. 1934. Ibid. **37**, 29.

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THE
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VOL. 10 SEPTEMBER 1959 NO. 2

CONTENTS

C. D. OLLIER. A Two-Cycle Theory of Tropical Pedology . . 137

S. A. RADWANSKI *and* C. D. OLLIER. A Study of an East African Catena 149

W. E. CALTON. Generalizations on Some Tanganyika Soil Data . 169

B. W. AVERY, I. STEPHEN, G. BROWN, *and* D. H. YAALON. The Origin and Development of Brown Earths on Clay-with-Flints and Coombe Deposits 177

T. A. JONES. Soil Classification—a Destructive Criticism . . 196

J. C. C. ROMANS. Some Measurements of Air Space in Scottish Soils 201

MARGARET G. DETTMANN *and* W. W. EMERSON. A Modified Permeability Test for Measuring the Cohesion of Soil Crumbs . . 215

W. W. EMERSON *and* MARGARET G. DETTMANN. The Effect of Organic Matter on Crumb Structure 227

W. W. EMERSON. The Structure of Soil Crumbs 235

D. S. JENKINSON *and* J. TINSLEY. Studies on the Organic Material Extracted from Soils and Composts. I. The Isolation and Characterization of Ligno-Proteins from Compost 245

J. D. S. GOULDEN *and* DAVID S. JENKINSON. Studies on the Organic Material Extracted from Soils and Composts. II. The Infra-Red Spectra of Ligno-Proteins Isolated from Compost 264

C. B. COULSON, R. I. DAVIES, *and* E. J. A. KHAN. Humic-Acid Investigations. II. Studies in the Fractionation of Humic Acids . 271

D. J. GREENLAND *and* P. H. NYE. Increases in the Carbon and Nitrogen Contents of Tropical Soils under Natural Fallows . 284

M. SCHNITZER. Interaction of Iron with Rainfall Leachates . 300

R. M. TAYLOR. Amorphous Iron Oxides in Soils 309

K. SHAW. Determination of Organic Carbon in Soil and Plant Material 316

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